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Field Study to Obtain Trace Element Mass Balances at Kingston Steam Plant

Tennessee Valley Authority
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FIELD STUDY TO OBTAIN TRACE ELEMENT MASS BALANCES AT KINGSTON STEAM PLANT

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16. ABSTRACT
The report gives results of a study to help characterize the various waste streams by identifying the mass flow rates of the minor and trace elements in each waste stream of a coal-fired utility boiler. In obtaining the mass balances for 28 elements, the inlet and outlet flows associated with three major pieces of equipment were used: the pulverizer, boiler, and electrostatic precipitator (ESP); Kingston Unit 6 has two ESPs. Thus, the mass balance presented reflected a good picture of Unit 6 at near-full-load operation. The mass imbalance for the entire system ranged from -12.5 to +6.3%. However, the mass imbalance for each element was quite different: in many cases, it greatly exceeded + or -12.5%. Nevertheless, 10 elements--Al, Be, Ca, Cr, Fe, Mg, S, Si, Ti, and V--had imbalances of < + or -10%; these elements represented about 93% of the total fly ash and bottom ash mass flow rates. Improved sampling for elements in the vapor phase is needed because most concentrations were below detection limits. Improved sampling for both the bottom ash and inlet to the mechanical collector would drastically improve the mass flow rate estimates and remove some of the assumptions of this report.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Properties	Pollution Control	13B	14G
Boilers	Analyzing	Stationary Sources	13A	14B
Utilities	Wastes	Mass Balances		
Coal	Fly Ash	Characterization	21D	21B
Trace Elements	Ash Content	Waste Streams	06A	
Chemical Analysis	Sampling	Bottom Ash	07D	

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ABSTRACT

This work was conducted to help characterize the various waste streams from a coal-fired utility boiler by identifying the mass flow rates of the minor and trace elements in each waste stream. The information was used to obtain a mass balance for 28 elements. Thus, the mass balance presented reflects a good picture of a 180-MW wet bottom boiler under near full load operating conditions. This work shows that improvements in the sampling technique for elements in the vapor phase is needed because most of the concentrations were below the detection limits. Improvements in the techniques used to sample both the bottom ash and inlet to the mechanical collector would drastically improve the mass flow rate estimates and remove some of the assumptions used in this report.

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TABLE OF ABBREVIATIONS

AAF	American Air Filter
acfm	actual cubic feet per minute
Alk	Alkalinity
A&MF	Ash and Moisture Free
BA	Bottom Ash
cm	10^{-2} meter
DS	Dissolved Solids
ESP	Electrostatic Precipitator
gpm	gallons per minute
h	hour
ℓ	liter
MC	Mechanical Collector
mg	10^{-3} grams
MW	10^{6} Watts
NS	Not Significant
ORP	Oxidation Reduction Potential
RC	Research-Cotterell
SASS	Source Assessment Sampling System
μm	10^{-6} meters or 1 micron
μmho	10^{-6} units of conductance

CONVERSION TABLE

A list of conversion factors for British units used in this report is as follows:

British	Metric
1 micron	10^{-6} meters
1 inch	2.54 centimeters
1 foot	0.3049 meter
1 mile	1.609 kilometers
1 pound	0.454 kilogram
1 ton (short)	0.9072 metric tons
1 gallon	3.785 liters

EXECUTIVE SUMMARY

This report is a summary of the sampling program that was undertaken at Kingston Steam Plant (unit 6). It was a complete mass balance study intended to help characterize the various waste streams, i.e., gas, liquid and solid waste, of a dry bottom coal-fired utility boiler.

Sampling points were established around each of the following major pieces of equipment at this coal-fired steam plant--pulverizer, boiler, and both electrostatic precipitators. At these sampling points, the mass flow rates and the concentrations of 29 elements were determined. The determinations included vapor samples from the flue gas duct although the vapor phase flows were not used in the mass balance calculations. The exception was sulfur because most concentrations were below detection limits and the number of vapor phase tests were extremely limited (see section on data reduction and treatment of concentrations below detection limits). The mass imbalance for the entire system ranged from -12.5 to +6.3 percent. The mass balance for each element was quite different. However, the following 10 elements--Al, Be, Ca, Cr, Fe, Mg, S, Si, Ti, and V--had an imbalance of less than 10 percent and represent approximately 93 percent of the total mass flow rate in the fly and bottom ashes.

The size distribution of fly ash was also considered. Cascade impactors were used to evaluate the size distribution of the fly ash particles. The samples from the cascade impactor were combined to allow chemical analysis for three ranges of particle sizes--<1 μm, 1 to 3 μm and >3 μm. The large amount of scatter prevents firm conclusions regarding much of the chemical analysis data. However, some trends can be pointed out for the reader's consideration. The elements Al, Fe, Mn, Ni, and Se generally had higher concentrations in the larger particle ranges while Na and Ca had higher concentrations in the lower ranges.

The liquid sampling during this project involved determining the bottom ash and fly ash flow rates from a flume that attached to the pipes on the inlet of the ash pond. This sampling procedure also required that the inflow sluice water be analyzed as well as the transport water to provide adequate background water quality data for the associated mass flows of each element in the water portion of the sampling program. It should be noted that the data from the air portion of the project (e.g., flue gas analysis) were used to calculate the mass flows if they conflicted with data from the water portion because the air portion data were obtained by more accurate standard methods.

SECTION 1

INTRODUCTION

Interest in coal combustion research has increased in recent years due, partly at least, to concern for the environmental effects of coal combustion products. It is only recently, however, that such power plants have been suspected as a source of potential toxic substances that exist in vapor or particulate form in the atmosphere or in aquatic ecosystems. Because fossil fuels are known to contain a multitude of chemical species that may be discharged into the environment as combustion products, and because the use of coal is expected to increase during the next two or three decades, attention is being given to obtaining information on the contribution of power plants to the environmental loading of these chemical substances. This may in turn lead to the refinement of means to control their discharge to the environment.

In a continuing effort to characterize waste products from coal-fired steam-electric generating plants, an extensive mass balance survey was conducted on TVA's Kingston Steam Plant Unit 6. This survey was the second in a planned series for characterizing the waste products from several types of boilers. One task from each of the following projects, "Characterization of Effluents from Coal-Fired Utility Boilers" and "Fly Ash Characterization and Disposal," make up this research effort. The "Characterization of Effluents" task was concerned with atmospheric emission of trace constituents in coal. The "Fly Ash Characterization" task was concerned with the constituents of liquid and solid effluents from the unit.

SECTION 2

MAJOR RESULTS AND CONCLUSIONS

The following conclusions are based on the 9-day field study conducted on a TVA steam plant (Kingston). The test boiler was a tangentially fired utility boiler rated at 200 MW.

- The mass balance around the pulverizer accounts for approximately 94 percent of the substance in coal. After making appropriate allowances for oxygen and silica content, the sum of the 28 trace elements considered in this study closely approximates the ash content of coal.

- Given the perfect balance on a total ash basis, balances were computed for all measured elements and for all elements (except sulfur) aggregated. The balances for the aggregated case for the various test days ranged from 87.5 to 106.3 percent, with an average of 96.7 percent. Average balances for the major elements were 94.2 percent for sulfur (excluding an anomalous 172 percent from the average), 103.7 percent for iron, 99.8 percent for silicon, 96.5 percent for aluminum, 90.2 percent for calcium, and 79.2 percent for potassium.

- Most of the elements tend to deposit in the pyrite and waste streams in the same relative proportions as the total ash composition. Other than elements that are considered volatile (e.g., F, Cl, Hg, Se, Sb), only cadmium exhibited preferential deposition, with about 25 percent of this element occuring in ash in the ESP hoppers.

- Measured ash flow rates from sluiced ash streams were determined to be unreliable because mass closure on the total ash for the unit approached 50 percent. This was not considered to be an adequate method for measurement of the sluiced ash.

- Fly ash had a much more pronouced effect on the raw sluice water quality than did the bottom ash. After transporting the ash to the pond, the fly ash sluice water showed increases in conductivity and in the concentrations of dissolved barium, boron, selenium, arsenic, copper, aluminum, silicon, and iron; whereas the bottom ash sluice water had lower concentrations of dissolved barium and silicon.

SECTION 3

RECOMMENDATIONS

1. Since the product formed by ashing coal in the laboratory could be qualitatively and quantitatively different from that formed in a boiler, false estimates of total ash flow rates may result. It is recommended that work be done to determine if differences exist and if they are significant.

2. Sampling procedures need to be improved for these elements--F, Cl, Hg, Se, Sb, and Ag. Large amounts of these elements are unaccounted for in the mass balance. Ag had a large number of below detection limit values recorded and some samples (e.g., outlet of the AAF ESP) were too small to analyze for Ag. The remaining elements are volatile at combustion temperatures and would be expected to be found in gaseous form at very low concentrations.

3. Variability of power plant operating conditions is a factor that must be recognized. In order to identify the behavior of trace elements under these various conditions, a longer sampling program is recommended. This longer program should add enough days to achieve a temporal arrangement of sampling occasions one day apart, two days apart, etc., to quantify the time dependanceies in power plant data.

4. The ability to accurately measure flow rates around the boiler (e.g., air preheater outlet and bottom ash) could drastically improve the mass balance estimates and, hence, the understanding of the behavior of trace elements through the system.

5. Establish a series of checks and balances that could be done in the field to improve the reliability of the data collected.

SECTION 4

APPROACH

This study began in July 1977, at Tennessee Valley Authority's Kingston Steam Plant located in East Tennessee at the base of a peninsula formed by the Clinch and Emory Rivers. TVA personnel conducted all sampling efforts during this study with the exception of the SASS train, which was operated by Monsanto.

All tests were conducted with the unit at steady operating conditions near full load (approximately 180 MW) throughout each daily test period. The unit was brought to test conditions approximately two hours before each daily test. All ash-cleaning operations were conducted prior to the test setup for each test.

TEST SITE DESCRIPTION

At the time of Kingston Steam Plant's completion in the mid-fifties, it was the largest known steam-electric plant in the world, with a total capacity of 1600 MW. Since its completion, various modifications have provided for an increase in the total output capacity of today's 1723 MW. The average coal consumption for the plant is about 4.2 million tons per year, which produces about 650 thousand tons of ash.

The plant uses about one million gpm of once-through cooling water, which is taken from the Emory River approximately 1.8 miles above its junction with the Clinch River. Although the intake structure is located on the Emory River, the actual intake water is drawn from the Emory River in the colder months of the year and from the Clinch River during the warmer months (Figure 1). An underwater dam, located below the confluence of the Clinch and Emory Rivers, causes the cooler Clinch River water to flow as an underwater density current up the Emory River to the plant intake structure. The Emory River water is warm in the summer months and thus flows over the cooler Clinch River water. This phenomenon creates for a seasonal water quality variation. This variation in water quality does not affect plant operations for cooling water usage; however, it does have a noticeable effect on the quality of the ash sluicing water.

TEST BOILER DESCRIPTION

The Kingston Steam Plant Unit 6 steam-electric unit uses a Combustion Engineering, Inc., reheat twin-dry bottom boiler to produce steam at 1,280,000 lb/h continually and a 4-hour peak rating of 1,410,000 lb/h. The boiler unit consists of two separate, but identical, furnaces with primary stages of superheater surfaces, reheat surfaces, and economizer surfaces. One side of the boiler is designated as the superheater furnace; the other side is designated as the reheat furnace. The steam from the boiler drives a General Electric Company turbogenerator, which has a nameplate capacity of 200,000 kW.

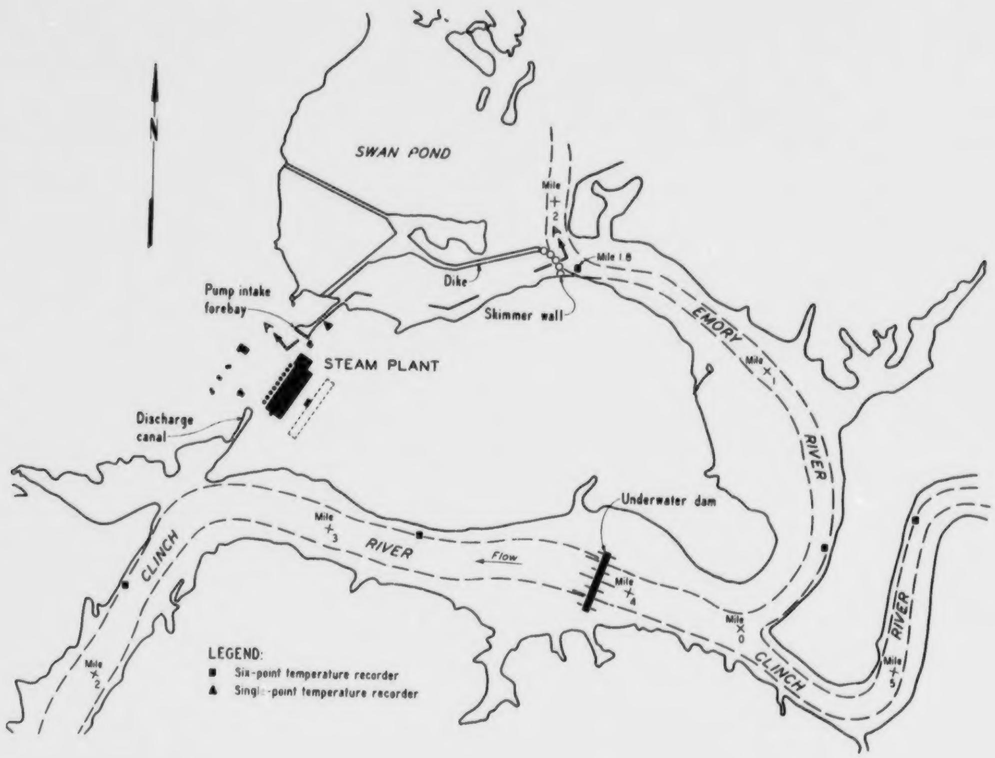

N
SWAN POND
Mile 2
Mile 1.8
Dike
Skimmer wall
Pump intake forebay
STEAM PLANT
Discharge canal
EMORY RIVER
Mile 1
Underwater dam
CLINCH RIVER
Mile 3
Flow
Mile 4
Mile 0
CLINCH RIVER
Mile 5
Mile 2
LEGEND:
■ Six-point temperature recorder
▲ Single-point temperature recorder

Figure 1. Location map of underflow diversion works.

The test boiler (Figure 2) is equipped with a coal bunker which supplies coal to six coal scales set to dump automatically at 500 lb per dump. Each scale has an hourly capacity of 30 tons and is designed for an accuracy of 1/4 of 1 percent. Bypass arrangements are built into the scales to assure a continuous supply of coal to the boiler in the event of a scale malfunction. The coal dumped from the scales falls through ducts into a Raymond bowl mill-type pulverizer. The plant is designed so that each scale supplies coal to a pulverizer located directly beneath the scale. Each of the six pulverizers has a capacity of 35,600 lb/h. The coal is pulverized to a design value grindability index of 50, and a moisture content of 7 percent.

As the coal is being pulverized, pyrites are rejected and are collected in hoppers located adjacent to each pulverizer. The pyrites are removed from the hopper by high pressure water operated exhausters which force them through a clinker grinding device and on through transport ducts to the settling basin. After being pulverized, the coal is transported from each pulverizer through four 12-inch outside-diameter pipes to the burners located in the sidewall corners of both the superheater and reheater sides of the boiler. To obtain uniform distribution of the coal in the pipes, a riffle type distribution is provided at each pulverizer exhauster outlet. Orifices are also provided in the coal pipes to equalize the friction.

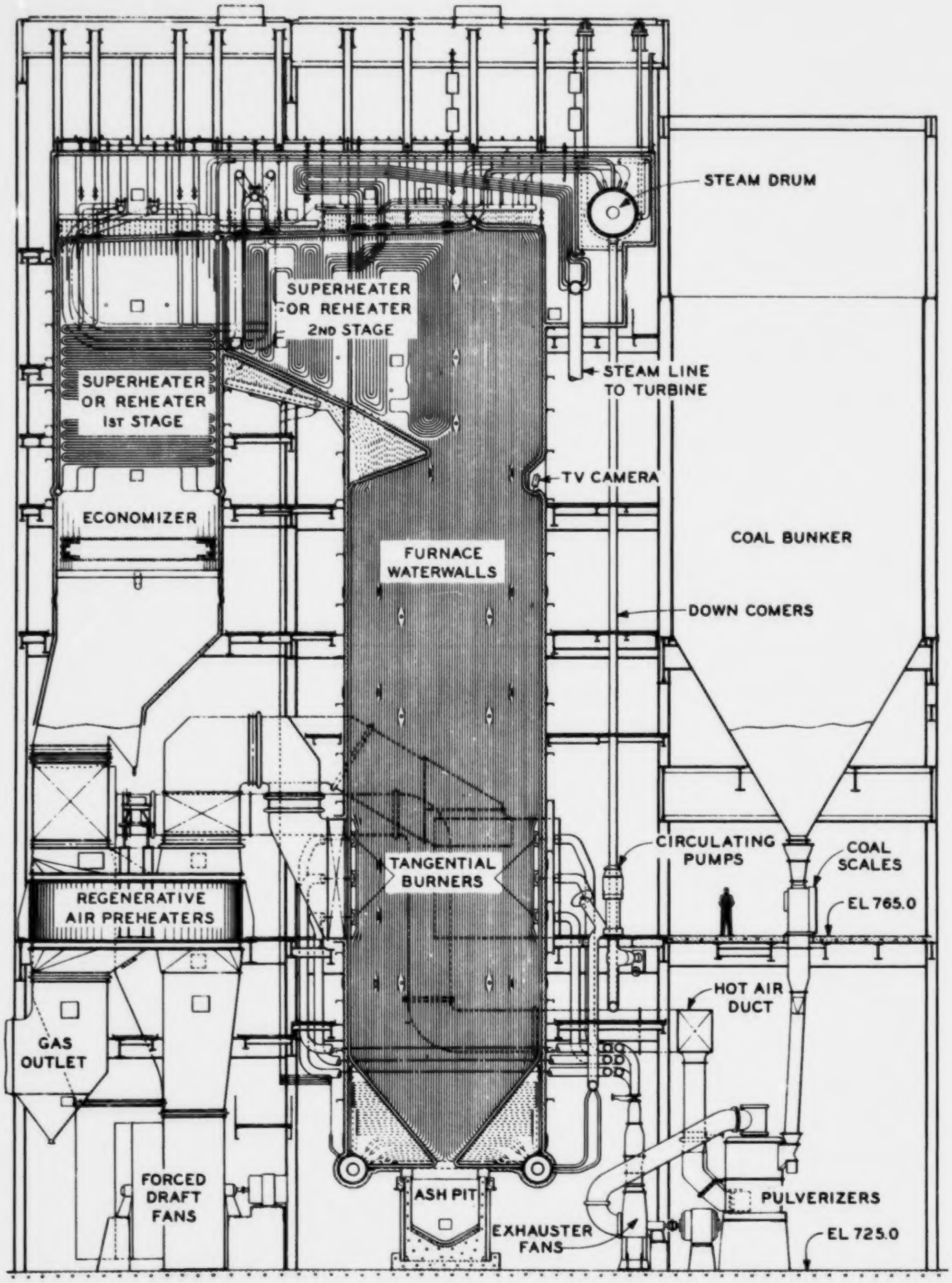

STEAM DRUM
SUPERHEATER OR REHEATER 2ND STAGE
SUPERHEATER OR REHEATER 1ST STAGE
STEAM LINE TO TURBINE
TV CAMERA
ECONOMIZER
COAL BUNKER
FURNACE WATERWALLS
DOWN COMERS
CIRCULATING PUMPS
COAL SCALES
TANGENTIAL BURNERS
REGENERATIVE AIR PREHEATERS
EL 765.0
HOT AIR DUCT
GAS OUTLET
FORCED DRAFT FANS
ASH PIT
PULVERIZERS
EXHAUSTER FANS
EL 725.0

Figure 2. Block diagram for Kingston Steam Plant Unit 6 coal and ash handling system.

Coal from three of the pulverizers feeds the superheater boilers, while the other three pulverizers feed the reheater boiler. There are twelve burners in each twin boiler--three in each sidewall corner. The burners are the adjustable, tangential type, and are provided with air-mixing chambers, adjustable air dampers, and connections for the coal pipes.

The combustion of the pulverized coal in the boiler produces waste byproducts in the form of gases and solids. The gases exit the top of the boiler and flow through a transport duct system on its way to the stack from which it is emitted to the atmosphere. The solid byproducts are further classified as bottom ash and fly ash.

The bottom ash falls to the bottom of the furnaces where it is collected to be sluiced to the settling pond. Each of the twin furnaces has separate clinker grinders and sluice systems. High pressure water jets are used to wash the ash from the bottom of the furnace into the clinker grinders. After the bottom ash passes through the clinker grinders, it is jetted to the settling pond through transport ducts by a high pressure water exhauster. Both the reheat and superheat bottom ashes are sluiced to the settling pond through a common sluice pipe.

Fly ash consists of those solid particles that are usually small in size and have a density that allows them to be entrained in the hot gas stream that exits the top of the boiler. After leaving the top of the boiler, the hot gas stream with the entrained fly ash passes through an economizer and then into an air preheater (Figure 2). The air preheaters are designed for a corrected gas temperature of 300°F with an entering air temperature of 80°F. As the hot gas stream flows through the air preheaters, it experiences direction and velocity changes; thus, the larger, heavier entrained fly ash particles fall out of the stream into collecting hoppers that are located beneath the air preheater. This fly ash is removed from the hoppers at regular intervals and transported to the settling basin by high pressure water exhausters.

After passing through the air preheaters, the gas stream containing the remaining fly ash passes through a mechanical fly-ash collector system. About 50 percent of the total fly ash is removed as the hot gas flows through these collectors. The fly ash removed by these mechanical collectors falls into hoppers that are located beneath the collectors. High pressure water exhausters are used to remove the fly ash from the hoppers and force it through transport ducts to the settling pond. The mechanical fly ash collectors are designed for a maximum normal gas flow of 310,000 cfm at 395°F, with a 3-inch water pressure drop.

After leaving the mechanical collectors, the gas stream then flows through a Research-Cottrell double-chamber electrostatic precipitator fly ash collector. About 45 percent of the total fly ash is removed from the gas stream at this point. The fly ash removed from the gas stream by these electrostatic precipitators collects in hoppers that are located beneath the precipitators. Removal of the fly ash from these hoppers is accomplished, at regular intervals, by a high pressure water exhauster system.

After leaving the Research-Cottrell electrostatic precipitator, the gas stream flows through an American Air Filter (AAF) electrostatic precipitator. Only about 4 percent of the total fly ash is removed by the AAF electrostatic precipitator. Removal of the fly ash from the hoppers is accomplished in a similar way to that collected by the Research-Cottrell electrostatic precipitator. After leaving the AAF electrostatic precipitator, the gas stream flows upward through the 1000-foot stack into the atmosphere.

SAMPLING PROCEDURES

Two different sampling efforts were carried out simultaneously during this test program. One effort focused on the gaseous and particulate emissions from the boiler. The second effort was directed at characterizing the ashes that were removed from the process at various points in the system. Figure 2 is a block diagram of the process with the sampling points identified. Table 1 is a summary of the samples taken and the chemical constituents or parameters for which they were analyzed. Table 2 is a listing of the trace elements investigated. The two efforts overlapped at both ESP's, where only one sample of the hopper ash was taken.

Because of financial constraints, the gaseous emissions study was conducted on only one-half the unit--the superheat side; and hopper ash samples were, therefore, taken on only that half of the ESP. The ash characterization effort took a sample across the entire unit. The following material is a description of the sampling procedures used at each sampling point identified in Figure 3.

Whole Coal

The whole coal samples were taken from each of the six coal scales serving the test boiler. A sampling ladle was used to collect a grab sample from each scale at 15-minute intervals during each daily test period. Two sets of samples were collected--one set taken from scales A, B, and C represented coal flowing to the superheat boiler only; and the other set taken from scales A, B, C, D, E, and F represented the total coal flowing to both the superheat and reheat boilers.

All the grab samples were put in large, plastic containers. At the end of each day the two samples were ground and then riffled into proportional homogeneous daily samples--one representing coal from scales A, B, and C; the other representing coal from scales A, B, C, D, E, and F. These daily samples were put in glass jars and delivered to the TVA Water Quality Branch's Units Operational Laboratory to be stored for future laboratory analysis. The total coal flow samples represented by the grab samples from scales A, B, C, D, E, and F were collected as backup samples for the pulverized coal samples.

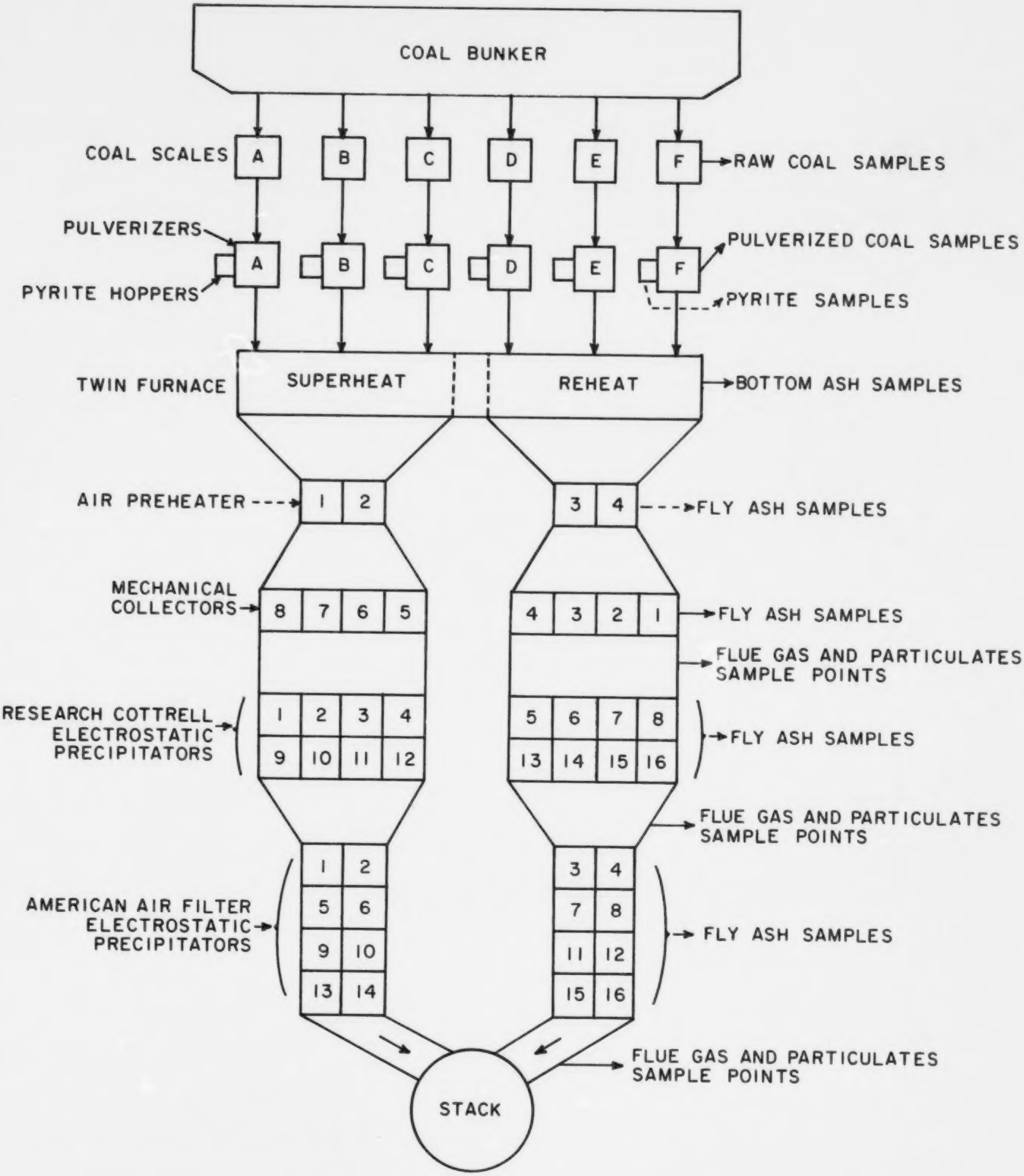
TABLE 1. SUMMARY OF SAMPLES AND CONSTITUENTS DETERMINED

Sample	Constituents Analyzed
Coal	Trace elements,* proximate and ultimate analysis
Pyrites	Trace elements
Bottom Ash, dry ash	Trace elements, major oxides (Al, Ca, Fe, K, Mg, Na, S, Si, and Ti)
, 14 hour supernatant	Trace elements, SO_4, pH, Alk, ORP, Conductivity
Boiler Outler	CO, O_2, SO_2, NO-NO_x
Mechanical Collector Ash	Trace elements, major oxides
ESP Ash, dry hopper ash	Trace elements
, 14 hour supernatant	Trace elements, SO_4, pH, Alk, ORP, Conductivity
ESP Inlet Ducts, total particulate	Trace elements (except Si)
, Vapor phase	Trace elements (except Si)
, Particulate sizing	Trace elements (except S, Si, Cl, F, Ag, Tl)
ESP Outlet Duct, total particulate	Trace elements (except S, Si)
, Vapor phase	Trace elements
, Particulate sizing	Trace elements (except S, Ag, Tl)
Raw Sluice Water, total	Trace elements, SO_4, SS, pH, Alk, ORP, Conductivity
, dissolved	Trace elements, SO_4, TDS

*Trace elements under consideration are listed in Table 2.

TABLE 2. MINOR AND TRACE ELEMENTS IN COAL

Aluminum (Al)
Antimony (Sb)
Arsenic (As)
Barium (Ba)
Beryllium (Be)
Boron (B)
Cadmium (Cd)
Calcium (Ca)
Chlorine (Cl)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)
Fluorine (F)
Iron (Fe)
Lead (Pb)
Magnesium (Mg)
Manganese (Mn)
Mercury (Hg)
Nickel (Ni)
Potassium (K)
Selenium (Se)
Silicon (Si)
Silver (Ag)
Sodium (Na)
Sulfur (S)
Thalium (Tl)
Titanium (Ti)
Vanadium (V)
Zinc (Zn)


COAL BUNKER
COAL SCALES
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B
C
D
E
F
RAW COAL SAMPLES
PULVERIZERS
PYRITE HOPPERS
A
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PULVERIZED COAL SAMPLES
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TWIN FURNACE
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FLY ASH SAMPLES
FLUE GAS AND PARTICULATES SAMPLE POINTS
STACK

Figure 3. Block diagram for Kingston Steam Plant Unit 6 coal and ash handling system

Pulverized Coal

As the whole coal is fed into each of the bowl mill pulverizers, it is pulverized to a design value grindability index of 50. Also, as the coal is ground, pyrites are rejected and collected in hoppers that are located adjacent to the pulverizers.

Samples of the pulverized coal were taken from each pulverizer. Two sampling ports, which are 90 degrees apart and located at the top of the pulverizer exhauster just before the transport ducts branch out to the burners, provided a place for collecting representative pulverized coal samples. Sampling was accomplished by traversing the duct at 90 degrees with a cyclone sample train. The sampling schedule provided for a sample to be taken at 5-minute intervals and rotated through the six transport ducts. Thus, each duct was sampled at 30-minute intervals during each daily test period. After each sample was taken from a duct, a 3/4-inch inside diameter stainless steel proportional sample splitter was used to take a homogeneous sample from the sampler jar and place it in a large glass jar to provide one daily sample. Two sets of samples were collected--one represented coal flowing to the superheater boiler (pulverizers A, B, C) only; the other represented coal flowing to both the superheater and reheater boilers (pulverizers A, B, C, D, E, F). All the pulverized coal samples were sent to the TVA Water Quality Laboratory for chemical analysis.

Pyrites

A sampling ladle was used to collect a grab sample from each of the six hoppers serving the six pulverizers. One grab sample was taken from each hopper just prior to the pyrites being sluiced to the settling pond. Before the samples were collected and the sluicing began, the pyrites in each hopper were leveled and a measurement of the depth of the pyrite in the hoppers was made. These measurements were used to calculate the total volume of pyrites collected during the daily test period. At the end of each day all the pyrite grab samples were combined, ground, and riffled to provide one daily sample. Due to budget problems, the daily pyrite samples were further combined to provide only three weekly samples. These daily samples were sent to the TVA Laboratory Branch for chemical analysis.

Pyrite slurry samples were collected as the pyrites were being sluiced to the settling pond. A sampling flume designed to provide a homogeneous sidestream from which representative grab samples could be taken was installed on the end of the transport pipe (Figure 4). The grab samples of the pyrite slurry were taken by pulling a 3-gallon plastic bucket up through the sidestream. The grab samples were taken at 15-second intervals during the entire sluicing period. All grab samples were poured into large, plastic containers where they were allowed to settle for 14 hours. After the settling period, the water was siphoned from the settled solids; the decanted volume was measured and again poured into another plastic container where it was well mixed, and then two water samples were collected.

TABLE 3. FIELD WATER QUALITY DATA

		Slurry Samples						Inflow Samples				
Date	Test No.	Temp.* (°C)	Cond. (µmho/cm)	DS (mg/1)	pH (units)	Total Alk (mg/1 as $CaCO_3$)	Acidity (mg/1)	Temp.* (°C)	Cond. (µmho/cm)	DS (mg/1)	pH (units)	Total Alk (mg/1 as $CaCO_3$)
Mechanical Collector												
7/19/77	114	30	290	310	8.9	90	0.3	26.5	203	212	8.0	80
7/20/77	115	28.1	268	272	7.2	58		28.5	203	202	7.5	62
7/21/77	116	26.2	311	311	7.8	85		26.4	189	200	7.9	83
7/22/77	117	28	279	29	8.1	78		25	205	201	6.2	68
7/25/77	119	28	312	326	8.2	77		25	211	198	7.7	73
7/26/77	120	24.8	289	280	7.9	75		23	214	199	8.0	76
7/27/77	121	25.8	334	335	8.0	102		23.3	215	205	7.6	101
7/28/77	122	22.1	308	290	8.2	100		24	210	198	8.0	101
RC ESP												
7/19/77	114	29.8	360	370	6.6	36		25.8	215	208	7.9	80
7/20/77	115	29.2	459	459	5.0	-		27.8	204	202	7.3	61
7/21/77	116	26.8	390	380	7.01	25		27	194	200	8.1	84
7/22/77	117	27.3	440	440	6.9	12		24.5	205	202	6.3	72
7/25/77	119	27	442	460	6.3	20		24.5	213	205	7.8	72
7/26/77	120	23.5	402	340	7.3	39		23.2	216	200	8.0	77
7/27/77	121	24.9	525	500	6.1	20		25.2	200	200	7.7	97
7/28/77	122	22.1	447	430	6.3	16		24.5	210	199	7.9	101
Pyrite												
7/19/77	114	27.8	220	222	7.7	80						
7/20/77	115	27	221	223	6.2	53						
7/21/77	116	-	-	-	-	-						
7/22/77	117	-	-	-	-	-						
7/25/77	119	27.5	243	229	7.3	62						
7/26/77	120	23.8	204	222	7.3	94						
7/27/77	121	23.2	236	221	7.0	90						
7/28/77	122	22.7	230	208	7.5	97						

TABLE 3. (CONTINUED)

		Slurry Samples						Inflow Samples				
Date	Test No.	Temp.* (°C)	Cond. (μmho/cm)	DS (mg/l)	pH (units)	Total Alk (mg/l as $CaCO_3$)	Acidity (mg/l)	Temp.* (°C)	Cond. (μmho/cm)	DS (mg/l)	pH (units)	Total Alk (mg/l as $CaCO_3$)
Bottom Ash												
7/19/77	114	26.8	231	231	7.6	74		27.2	203	211	8.1	82
7/20/77	115	28	222	220	8.2	78		27.6	201	205	7.1	58
7/21/77	116	-	-	-	-	-		-	-	-	-	-
7/22/77	117	24.8	227	211	7.2	68		25.5	210	200	7.4	65
7/25/77	119	25.5	225	220	7.7	73		24.5	213	204	7.7	69
7/26/77	120	24	224	220	7.3	76		23.3	219	197	8.1	76
7/27/77	121	23.3	230	215	7.1	95		23.3	211	202	7.7	101
7/28/77	122	22.2	234	215	7.7	102		23.2	215	195	8.1	100
American Air Filter ESP												
7/19/77	114	32	510	610	5.0	-		27.5	217	210	8.0	80
7/20/77	115	27	502	490	3.1	-	0.1	27	202	209	7.2	58
7/21/77	116	25.1	499	480	5.3	0.4		26	184	198	7.8	82
7/22/77	117	28	441	450	4.8	-	0.1	24	212	200	7.8	67
7/25/77	119	26.8	503	480	3.9	-	0.2	25	210	208	7.8	73
7/26/77	120	23	399	379	5.0	-		22.5	204	200	8.2	75
7/27/77	121	27.5	349	379	5.3	0.4		24.5	199	205	7.7	95
7/28/77	122	21.5	490	459	4.7	-	0.3	23.7	221	189	8.1	100

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*Temperature of the sample when these field measurements were made.

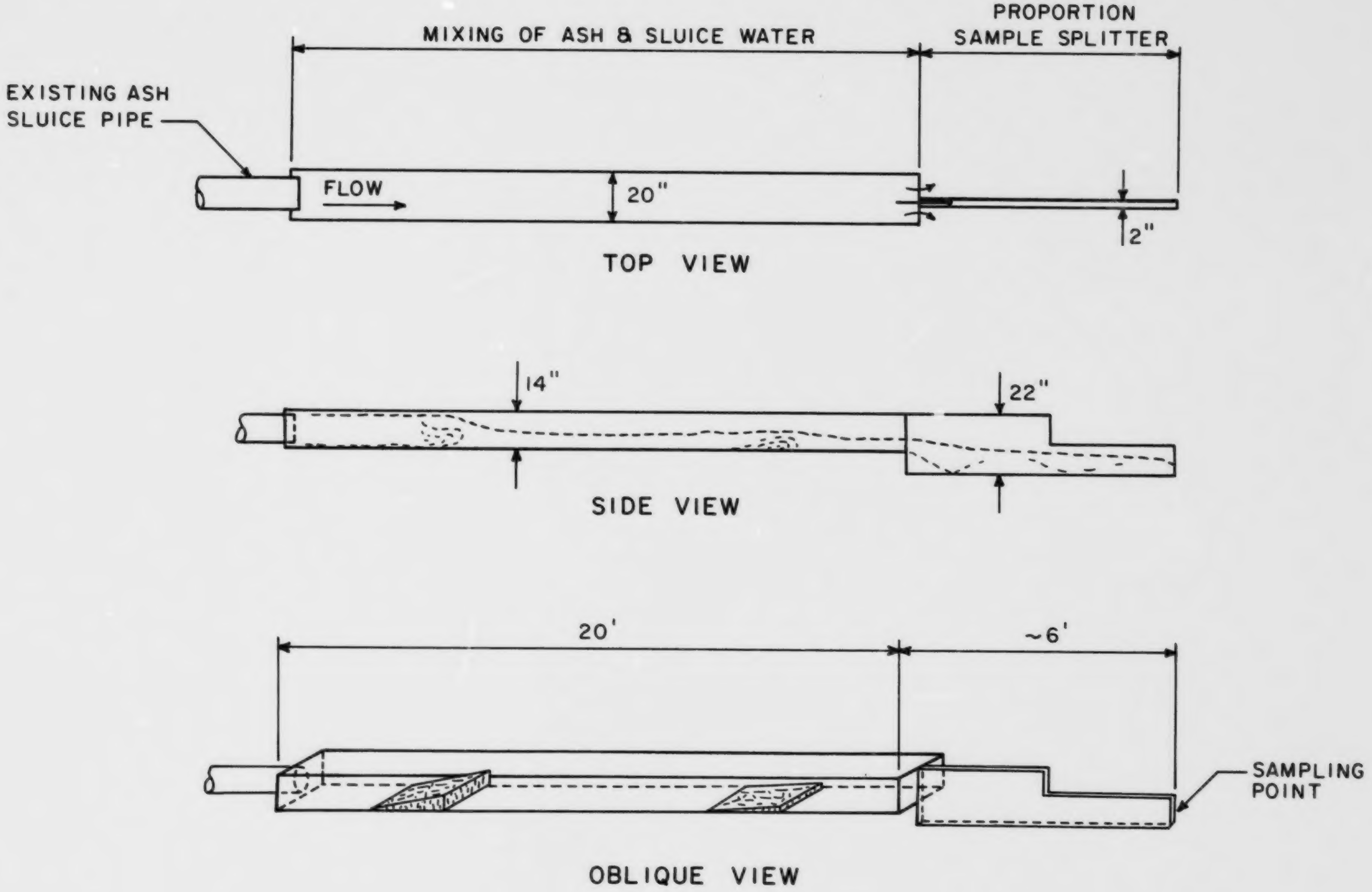

EXISTING ASH SLUICE PIPE
MIXING OF ASH & SLUICE WATER
PROPORTION SAMPLE SPLITTER
FLOW
20"
2"
TOP VIEW
14"
22"
SIDE VIEW
20'
~6'
SAMPLING POINT
OBLIQUE VIEW

Figure 4. Diagram of the bottom ash and pyrite sampling flume

One sample was used for the field water quality analysis for dissolved solids, pH, conductivity, oxidation reduction potential (ORP), and alkalinity (Table 3). The second sample was filtered through a 0.45 μ millipore filter, and the filtrate was poured into the various bottles containing preservatives for specific chemical analysis. These filtered samples were sent to the TVA Laboratory Branch for chemical analysis. The settled solids were put into plastic bags and delivered to the TVA Water Quality Branch's Units Operations Laboratory where they were dried and weighed. The supernate measurements and dried solids weights were used, along with the sluice flow rate for calculating the volume of pyrites sluiced. The calculated volumes are compared to the volumes calculated by using the hopper depth measurements in Table 4. These show very good correlation.

Bottom Ash

Bottom ash produced by the coal combustion fell to the bottom of the furnaces where it was collected and later sluiced to the settling basin. Collecting a daily representative grab sample from the bottom of the superheat or reheat furnace was infeasible; therefore, all bottom ash samples were taken from the slurry of ash being sluiced to the ash pond. Since the bottom ash and pyrites are transported to the settling basin through the same transport duct, the sampling flume designed to provide a homogeneous sidestream described in pyrite slurry sampling, served as well for the bottom ash slurry sampling (Figure 4). The sidestream flow of approximately 195 gallons per minute represented one-tenth of the total sluice flow. The bottom ash slurry samples were also taken by pulling a 3-gallon plastic bucket up through the entire sidestream overflow at 15-second intervals during the entire sluicing period for both the superheat and reheat furnaces. For each test, all the 15-second samples were combined in large, plastic containers and allowed to settle for 14 hours.

After a 14-hour settling period, all the water was siphoned from the settled solids and the decanted water volume was measured. A sample of the supernatant was filtered, using an 0.45 μ millipore filter, and sent to the TVA Laboratory Branch for chemical analysis. The supernatant was also analyzed by field personnel for pH, alkalinity, ORP, dissolved solids, and conductivity. The settled solids were put in plastic bags and delivered to the TVA Water Quality Branch's Units Operation Laboratory where they were air dried and then weighed. Then the ash was delivered to the TVA Laboratory Branch for chemical analysis. Before the solids samples were analyzed, they were ground to a minus 60-mesh in a Raymond bowl mill-type grinder. The 60-mesh meets the ASTM standard for coal analysis.

The dry bottom ash weights and the decanted water volume were used with the sluice flow rate (1949 gpm) to calculate the bottom ash sluiced. The sluice flow rate was measured with a TecSonic ultrasonic flow meter attached to the sluice pipe. The calculated bottom ash flows are reported in Table 5.

TABLE 4. PYRITE FLOW CALCULATIONS

Date	Test number	Weight of dry solids, lb.	Volume of H_2O collected, gal.	Sluice time, min.	Total test period, hr.	Pyrite flow rate, ton/hr.	Total pyrite sluiced, lb.	Total pyrite measured in hoppers, lb.	$\frac{\text{Collected-measured}}{\text{collected}}$ %
7/19/77	114	5.69	31.8	20.08	6.09	0.57	6943	5170	+26
7/20/77	115	5.49	27.8	19.75	5.13	0.73	7490	4805	+36
7/21/77	116	-	-	-	-			-	
7/22/77	117	-	-	16.25	5.77	-	-	5105	-
7/25/77	119	6.28	37.8	18.42	5.02	0.59	5823	4925	+15
7/26/77	120	4.59	28.5	14.92	5.84	0.40	4672	4135	+11
7/27/77	121	4.04	22.0	14.08	5.62	0.44	4954	4515	+9
7/28/77	122	3.99	28.8	15.08	5.03	0.40	4024	4560	-13

TABLE 5. BOTTOM ASH TEST DATA AND CALCULATED FLOW DATA

Date	Test number	Weight of dry solids, lb.	Volume of H_2O collected, gal.	Sluice time, min.	Total test period, hr.	Ash flow rate, ton/hr.
7/19/77	114	16.48	61.5	22.25	6.02	0.95
7/20/77	115	8.16	28.3	13.50	5.19	0.72
7/21/77	116	-	-	-	-	-
7/22/77	117	10.31	33.5	21.75	7.21	0.89
7/25/77	119	11.64	42.0	25.25	5.23	1.29
7/26/77	120	7.91	28.8	21.67	5.97	0.96
7/27/77	121	11.91	40.5	20.25	6.05	0.95
7/28/77	122	12.19	42.0	20.92	5.97	0.98

AIR PREHEATER FLY ASH COLLECTOR

The fly ashes collected in the air preheater system were very large particles that fell out of the hot gas stream due primarily to velocity changes. The volume of the ash collected in the hoppers could not be measured. Also, slurry samples could not be collected due to the very short total sluice time required for cleaning the four hoppers. Due to the problems encountered with the short sluicing period, dry samples were taken from sampling ports located in the bottom of the hoppers at approximately 15-minute intervals during the daily test period. The total ash collected in the hoppers is estimated to be a very small percentage of the total ash. Due to budget and because these samples contained a very small volume of ash, they were not analyzed or used during the analysis of the data.

MECHANICAL FLY ASH COLLECTOR (MC)

There are eight hoppers receiving fly ash from the mechanical collectors. Four hoppers serve the reheat furnace ducts and the other four serve the superheater furnace ducts. Samples of the MC fly ash were collected from the hoppers in the dry form, and another sample was collected as slurry as the ash was being sluiced to the ash ponds. The dry samples were taken from each hopper at 30-second intervals as each hopper was being emptied. Due to the great volume of fly ash collected in these hoppers and the physical design of the sluice system, the hoppers were sluiced continually, cycling through hoppers 1 through 8, with only a 3- to 4-minute lapse between cycles.

The sampling program provided for two sets of samples, one representing only the flow of fly ash from the superheater furnace, and the other providing one sample for the total flow from both furnaces. A thief sampler was used to take samples from sampling ports located in the bottom of each hopper. The samples collected during each sluicing cycle, which represented the superheater furnace only, were kept in separate containers; and at the end of each day, they were composited proportionally by weight based on the sluicing cycle durations to provide one daily sample. The bags representing both the superheater and reheater furnaces were also composited based on cycle duration. Both sets of samples were delivered to the TVA Laboratory Branch for chemical analysis.

MC slurry samples were collected at the end of the transport pipe as the MC fly ash was being sluiced to the ash pond. A plastic cup was used to collect approximately 200-ml grab samples at 15-second intervals during the sluicing operation. These grab samples were combined in large, plastic containers with a plastic bag liner and, after a 14-hour settling period, the water was carefully siphoned off and the decanted water volume was measured. This water was put into another container and, after being thoroughly mixed, two samples were taken--one to be used for field water quality analysis (Table 3); the other sample was filtered through an 0.45 μ millipore filter, and the filtrate was poured into bottles which contained preservatives for various chemical analysis. These samples were sent to the TVA Water Quality Laboratory for chemical analysis.

After the water was siphoned from the settled solids, they were put in plastic bags and delivered to the Water Quality Branch's Units Operation Laboratory to be dried, weighed, and stored for future laboratory analysis. The decanted water volume and the weight of the solids were used along with the sluice flow rate to calculate the total volume of the ash sluiced (Table 6). The sluice flow rates used in making these calculations were measured with an ultrasonic flow meter.

The fly ash from the MC hoppers of Units 5 and 6 was sluiced to the ash pond through the same pipe system. Therefore, the slurry samples for Unit 6 were collected only at such times when Unit 5 sluice could be turned off. Unit 5 could be turned off only when the fly ash in the hoppers was very low.

RESEARCH-COTTRELL ELECTROSTATIC PRECIPITATOR FLY ASH COLLECTORS (RC)

Since the high pressure water ejector used for pulling the RC fly ash from Unit 6 also serves Unit 5, the sluicing was accomplished intermittently between the two units. Sample collecting was carried out each time Unit 6 hoppers were emptied. Dry fly ash samples were taken at 15-second intervals with a thief sampler from sampling ports located in the bottom of each of the 16 hoppers. The sample collecting and handling was carried out the same as that described for the MC fly ash except for the number of samples. The first sample represented the total fly ash from the superheater furnace that was collected in the first four hoppers. The second sample represented the fly ash from the superheater furnace collected in hoppers 9 through 12. The third sample was a composite representing fly ash from hoppers 1 through 4, and 9 through 12.

Slurry samples of the RC fly ash were collected as it was being sluiced to the ash pond. A 200-ml plastic cup was used to collect a grab sample at 15-second intervals during the entire sluicing period. These slurry samples were composited in large, plastic containers and allowed to settle for 14 hours. Following the settling period, the handling process was the same as that described for the MC fly ash samples.

The field analyses are shown in Table 3, and the calculated flow rates are shown in Table 7.

AMERICAN AIR FILTER ELECTROSTATIC PRECIPITATOR FLY ASH COLLECTORS (AAF)

Dry fly ash samples were taken from the AAF hoppers by the same method as that used for collecting the MC and RC samples. However, the hoppers as constructed with four rows of hoppers and four hoppers per row did not catch equal amounts of ash as was the case with the MC and RC hoppers. During the 14 days of testing no good samples were collected from hoppers 1 through 4, and only an occasional trace was collected from hoppers 13 through 16. A good representative sample was taken from hoppers 5 through 8, and hoppers 9 through 12 provided only a small sample each day. Sample compositing and handling was similar to the dry RC samples.

TABLE 6. MECHANICAL COLLECTORS FLY ASH TEST DATA AND CALCULATED FLOW RATE

Date	Test number	Weight of dry solids, lb.	Volume of H_2O collected, gal.	Sluice time, min.	Total test period, hr.	Ash flow rate, ton/hr.
7/19/77	114	2.97	14.75	332.95	6.68	4.4
7/20/77	115	1.96	12.25	361.90	7.34	3.4
7/21/77	116	5.72	22.00	321.10	6.72	5.4
7/22/77	117	6.14	24.25	248.10	6.38	4.3
7/25/77	119	14.62	65.5	357.50	6.77	5.1
7/26/77	120	5.20	31.25	396.12	7.47	3.8
7/27/77	121	8.23	35.5	329.23	6.31	5.2
7/28/77	122	5.98	28.5	345.48	6.84	4.6

TABLE 7. RESEARCH-COTTRELL COLLECTORS FLY ASH TEST DATA AND CALCULATED FLOW RATE

Date	Test number	Weight of dry solids, lb.	Volume of H_2O collected, gal.	Sluice time, min.	Total test period, hr.	Ash flow rate, ton/hr.
7/19/77	114	11.81	27.5	176.9	6.17	4.6
7/20/77	115	19.86	52.0	185.2	6.87	3.8
7/21/77	116	24.91	68.0	201.8	7.12	3.9
7/22/77	117	13.59	37.5	162.8	5.81	3.8
7/25/77	119	15.32	54.5	199.1	7.03	3.0
7/26/77	120	18.28	56.0	188.1	6.48	3.5
7/27/77	121	20.53	60.5	149.9	5.24	3.6
7/28/77	122	21.98	63.5	175.6	6.29	3.6

Slurry samples were taken from the end of the AAF fly ash transport pipe at the ash pond. With the exception of the sampling frequency, which was continuous throughout the sluice period, the procedure and sample processing were the same as those for the MC slurry sampling program. Since these hoppers were emptied only once each day, the grab samples were taken continuously to ensure a good representative sample. The AAF slurry samples were handled the same as the MC and RC fly ash slurry samples. Flow measurements and sluice water quality for the AAF fly ash are shown in Tables 8 and 3, respectively.

INFLOW SLUICE WATER SAMPLES

Inflow sluice water samples were collected from each of the water supply pipes for each sluice system. These samples were taken from taps located in various pipes during each sluicing period for which slurry samples were being collected. The taps were adjusted to allow a small, continuous stream of water to flow into a 5-gallon plastic container. The sampling was started and stopped with each sluicing operation. At the end of each day, each sample was processed to provide a dissolved and suspended water sample for laboratory analysis. Also, a series of field analyses were made on these water samples.

Flow measurements were made on each of the ash and pyrite sluice systems. During the first week, a dye tracer was used for making these velocity measurements; but during the actual test, the velocity measurements were made by permitting a slug of clear water to flow through the sluice pipes prior to each sluicing operation. The black ash sluice water then served as the tracer for time of travel study. The flows calculated from the measured velocity and pipe area were much higher than the design flows. The only logical conclusion for the results is that the transport pipes do not flow full at all times or over the entire length (approximately 2000 feet) of the pipe.

An ultrasonic flow metering device was installed on the MC, RC, and AAF inflow sluice water lines, and the results of these measurements were used in calculating the sluice flow rates reported in Table 9.

Boiler Outlet Duct

The major gaseous components of the flue gas were measured at the boiler outlet with instruments installed on a mobile TVA van. These included a DuPont Model 400 nondispersive UV spectrophotometer for SO_2, a Thermo Electron model 10A chemiluminescent monitor for NO and NO_x, a Beckman Model 864 IR analyzer for CO and another for CO_2, and a Beckman Model 742 polarographic sensor for O_2. The CO_2 analyzer malfunctioned, and no data on this constituent was obtained; however, ORSAT measurements of CO, CO_2, and O_2 were made at the ESP inlet duct, which compared favorably with the van instrumentation measurements of CO and O_2. Five sampling probes to a common sample header were used to traverse the duct at the entrance to the air heater through five ports at three traverse points (depth) to draw representative samples. The samples were conveyed through

TABLE 8. AMERICAN AIR FILTER FLY ASH TEST DATA AND CALCULATED FLOW RATE

Date	Test number	Weight of dry solids, lb.	Volume of H_2O collected, gal.	Sluice time, min.	Total test period, hr.	Ash flow rate, ton/hr.
7/19/77	114	4.03	23.9	34.00	7.42	0.6
7/20/77	115	1.90	18.3	19.57	6.98	0.2
7/21/77	116	2.17	16.0	19.30	6.40	0.3
7/22/77	117	2.03	20.3	18.12	6.23	0.2
7/25/77	119	4.56	32.0	23.22	6.24	0.4
7/26/77	120	3.98	28.3	39.58	7.05	0.6
7/27/77	121	2.89	36.3	30.48	6.51	0.3
7/28/77	122	2.85	25.0	26.35	7.03	0.3

TABLE 9. SLUICE WATER FLOW RATES

	gpm
Pyrite	1949
Bottom ash	1949
Air preheater fly ash	875
Mechanical collector fly ash	875
Research-Cottrell fly ash	755
American Air Filter fly ash	1600

Teflon tubing to the instruments located in the van for measurements of SO_2, $NO-NO_x$, CO, and O_2. Gas monitoring at the boiler outlet was done simultaneously with the sampling efforts at the ESP inlet and outlet ducts.

Electrostatic Precipitator Inlet and Outlet Ducts

A number of different sampling techniques were utilized in sampling the ESP inlet and outlet ducts. A description of the equipment used can be found in Appendix A.

METHODS OF CHEMICAL ANALYSIS

A number of different chemical analyses were performed on the various samples taken during this test. The techniques used for the quantitative determinations were based on:

1. Atomic Emission Spectroscopy
2. Atomic Absorption
3. Gravimetry
4. Potentiometric Titration
5. Ion Chromatography
6. Specific Ion Electrode
7. Differential Pulse Anodic Stripping Voltametry
8. Colorimetry
9. Titrimetric Analysis
10. Turbidimetric Analysis

The procedures used are described in detail in Appendix B.

As a check on the chemical analysis procedures, certified NBS Standards 1632 coal and 1633 fly ash were analyzed in parallel with the test samples. (These data are presented in Appendix B.) Appropriate blanks were run on the various collection substrates to correct for trace elements contained in the substrates. An aliquot of each liquid reagent used in each sampling train was analyzed for trace elements. In each case the value obtained for an element in the blank was subtracted from the corresponding element in the test sample. If the sample value was not at least twice the value of the blank, the difference was reported as a "less than" number for that element.

SECTION 5

RESULTS AND DISCUSSION

The results obtained from these studies are presented in the following terms:

- Boiler Operating Conditions for Test
- Coal Analysis
- Characterization of Waste Streams
- Mass Balance

BOILER OPERATING CONDITIONS FOR TEST

During each test, all data on the unit operating conditions were obtained from the control room instrumentation on an hourly basis and were averaged for each parameter (Table 10).

OPERATIONAL AND TESTING SCHEDULE

The testing and sampling program was designed so as to allow phases of the daily operations around the test boiler to conform as closely as possible to the normal operating schedule. The sampling schedule covered about 8 hours of boiler operation on each day of testing. The load factors, about 90-percent capacity, for this boiler were set about 2 hours before each daily test started and remained essentially constant during the entire test day. Pretest ash cleaning operations were conducted in the morning prior to each test. Table 11 shows the pretest cleaning and actual testing and sampling times for each stream sampled.

COAL ANALYSIS

Since the composition of coal varies greatly from source to source and even within a single source (coal bed), the composition of ash and stack emissions can also vary greatly. The coal consisted of carbonaceous matter and a mixture of various minerals (shales, clays, sulfides, and carbonates).

Proximate analysis of the whole coal and pulverized coal samples is summarized in Tables 12 and 13. The results were essentially the same for both coal samples. Ultimate analysis of the pulverized coal is summarized in Table 14. In the ultimate analysis, oxygen is calculated by subtracting the sum of the percentages of moisture, ash content, carbon, hydrogen, and nitrogen from 100 percent.

The ash from the proximate analysis was analyzed for nine major elements, and the results are given as oxides of the elements in Table 15. The values for all oxides, except SiO_2, were obtained using standard analytical procedures. It was assumed that the nine oxides in Table 15 comprised 99.5 percent of the total residue. Since SiO_2 is extremely

TABLE 10. BOILER OPERATING CONDITIONS FOR TEST
(AVERAGE VALUES)

	Test								
	114	115	116	117	118	119	120	121	122
Load (MW)	182	182	181	180	180	182	179	181	182
Bar. Pressure (in. of Hg)	29.55	29.59	29.49	29.45	29.42	29.35	29.42	29.46	29.47
Air Flow 10^6 (lb/h)	1.17	1.18	1.15	1.14	1.13	1.15	1.12	1.13	1.15
Steam Flow 10^6 (lb/h)	1.11	1.11	1.10	1.10	1.10	1.12	1.09	1.09	1.10
Pulverizer A (Amps)	42	41	41	42	43	42	43	43	41
B	42	42	40	42	43	42	43	42	39
C	40	40	42	41	44	43	41	41	43
D	44	45	44	44	44	43	43	44	40
E	46	44	43	44	45	43	44	42	46
F	42	40	40	41	43	42	45	43	43
FD Fan A (Amps)	58	58	57	57	57	57	56	56	58
ID Fan A	136	140	141	138	134	133	134	129	131
FD Fan B	66	67	66	66	66	66	66	66	67
ID Fan B	158	165	154	154	152	148	140	145	149
Furnace Draft A (in. of H_2O)	-.56	-.54	-.65	-.55	-.55	-.58	-.59	-.53	-.50
Furnace Draft B	-.45	-.43	-.44	-.41	-.41	-.46	-.39	-.40	-.39
Air Heater Diff. A (in. of H_2O)	4.2	4.4	4.4	4.3	4.2	4.1	4.1	4.1	4.0
Air Heater Diff. B	3.2	3.1	3.0	3.1	2.7	3.3	2.8	2.8	2.9
Gas Leaving AH A (°F)	335	340	345	342	335	338	340	335	337
Gas Leaving AH B (°F)	337	342	338	338	332	332	327	328	334

TABLE 11. PRETEST CLEANING AND ACTUAL TESTING TIMES FOR THE VARIOUS ASH STREAMS

		Pryite Sluicing Schedule							
		7-19-17	7-20-77	7-21-77	7-22-77	7-25-77	7-26-77	7-27-77	7-28-77
Test Number		114	115	116	117	119	120	121	122
Pretest Cleaning Sluice	Start	7:00:00	8:23:20	-	7:48:45	8:27:00	7:40:00	7:34:24	8:15:15
	Stop	7:30:45	8:50:00	-	8:04:30	8:43:05	7:50:42	7:41:30	8:27:00
Test Cleaning Sluice	Start	1:10:40	1:34:45	-	1:34:15	1:27:05	1:28:30	1:08:15	1:15:10
	Stop	1:30:45	1:54:30	-	1:50:30	1:45:30	1:43:25	1:22:20	1:30:15
		Bottom Ash Sluicing Schedule							
		7-19-77	7-20-77	7-21-77	7-22-77	7-25-77	7-26-77	7-27-77	7-28-77
Test Number		114	115	116	117	119	120	121	122
Superheater									
Pretest Cleaning Sluice	Start	7:33:30	8:51:15	10:15:55	7:15:00	8:46:05	7:51:57	7:42:47	7:36:37
	Stop	7:46:30	9:02:00	10:26:04	7:27:00	8:55:15	8:01:30	7:57:22	7:53:34
Test Cleaning Sluice	Start	1:38:40	2:07:45	-	2:27:30	2:00:00	1:54:00	1:50:00	1:43:20
	Stop	1:50:45	2:12:30	-	2:37:50	2:11:00	2:01:00	1:59:30	1:50:45
Preheater									
Pretest Cleaning Sluice	Start	7:50:13	9:04:30	10:29:25	7:28:00	8:59:25	8:05:29	7:59:05	7:56:47
	Stop	8:13:30	9:17:00	10:42:00	7:43:00	9:14:15	8:25:04	8:13:00	8:14:47
Test Cleaning Sluice	Start	1:54:50	2:15:30	-	2:43:50	2:12:30	2:03:20	2:02:00	1:53:40
	Stop	2:05:00	2:24:15	-	2:55:15	2:26:45	2:18:00	2:12:45	2:07:10

TABLE 12. PROXIMATE ANALYSIS OF WHOLE COAL

Test	114	115	116	117	119	120	121	122	AVG
% Moisture	3.0	3.3	3.4	3.9	2.1	3.6	3.3	3.4	3.3
% Ash	18.5	17.3	16.6	16.2	20.0	20.0	17.5	18.8	18.1
% Volatile Matter	32.8	32.3	32.7	33.3	33.2	32.5	33.2	37.7	32.8
% Carbon	48.7	50.3	50.6	50.5	46.8	47.6	49.4	48.6	49.1
% Sulfur	2.2	2.2	2.0	2.1	2.4	1.9	2.2	2.6	2.2
Btu/lb Dry	11759	12193	12284	12181	11535	11428	11824	11676	11860
Btu/lb A&MF	14427	14741	14735	14534	14430	14285	14324	14364	14480

TABLE 13. PROXIMATE ANALYSIS OF PULVERIZED COAL

Test	114	115	116	117	119	120	121	122	AVG
% Moisture	2.2	2.0	1.7	2.2	2.3	2.4	2.2	1.9	2.1
% Ash	18.7	17.5	17.2	15.7	19.8	19.0	17.1	17.9	17.9
% Volatile Matter	32.6	32.5	32.9	33.2	33.0	32.3	32.9	32.3	32.7
% Carbon	48.8	50.1	50.0	51.2	47.3	48.8	50.1	49.8	49.5
% Sulfur	2.2	2.1	2.2	2.1	2.3	1.7	2.1	2.3	2.1
Btu/lb Dry	11815	12054	12228	12358	11610	11680	12085	12014	11980
Btu/lb A&MF	14529	14601	14757	14657	14476	14421	14563	14632	14579

TABLE 14. ULTIMATE ANALYSIS OF PULVERIZED COAL

Test	114	115	116	117	119	120	121	122	AVG
% Carbon	66.3	68.1	68.8	69.4	65.0	66.1	68.1	67.4	67.4
% Hydrogen	4.7	4.7	4.7	4.7	4.6	4.6	4.7	4.7	4.7
% Nitrogen	1.6	1.6	1.7	1.5	1.6	1.5	1.5	1.6	1.6
% Oxygen*	6.7	6.1	5.6	6.7	6.9	7.3	6.8	6.4	6.6

*Note: Percent oxygen is obtained by difference and was not directly analyzed.

TABLE 15. MAJOR ELEMENTS (GIVEN AS OXIDES) OF ASH PRODUCED IN THE LABORATORY BY FIRING COAL AT APPROXIMATELY 800°F

Test	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Total
114	54.2	26.0	11.0	1.3	1.2	1.5	0.4	2.7	1.2	99.5
115	53.2	25.8	12.0	1.4	1.2	1.7	0.3	2.7	1.2	99.5
116	52.6	25.7	12.5	1.6	1.2	1.7	0.3	2.7	1.2	99.5
117	56.0	24.0	11.3	1.4	1.2	1.7	0.5	2.5	0.9	99.5
119	56.0	24.5	10.9	1.3	1.3	1.5	0.5	2.6	0.9	99.5
120	59.2	24.4	8.4	1.0	1.2	1.2	0.6	2.5	1.0	99.5
121	56.8	23.8	10.9	1.4	1.2	1.5	0.4	2.5	1.0	99.5
122	56.1	24.1	11.5	1.4	1.2	1.4	0.5	2.4	0.9	99.5

difficult to measure chemically, SiO_2 was determined by subtracting the sum of the other eight oxides from 99.5 percent.

Both the whole coal and pulverized coal samples were ashed prior to trace element analysis according to ASTM Standard D3174. The coal samples were analyzed for the trace elements listed in Table 2. These data were combined with the proximate and ultimate analysis to provide an additional check on the balance of elements in the coal. The sum of the trace elements, carbon, hydrogen, nitrogen, oxygen, and moisture is shown to represent 94 percent of the total coal (Table 16).

The results of the trace element analysis of coal are reported in Table 17. The three predominate elements in coal, excluding sulfur, are silicon, aluminum, and iron; these 3 elements comprise approximately 74 percent of the total mass of elements. Calcium, magnesium, potassium, sodium, chlorine, oxygen, and titanium comprise an additional 16 percent. The remaining trace elements provide less than 1 percent of the total mass of elements.

TABLE 16. CHEMICAL BALANCE AROUND THE PULVERIZED COAL USING TRACE ELEMENT ANALYSIS AND ULTIMATE ANALYSIS OF COAL

Test	114	115	117	119	120	121	122
Sum of 28 Trace Element Concentrations (%) in Pulverized Coal*	12.65	11.38	10.78	12.43	11.97	11.17	11.63
Carbon**	66.3	68.1	69.4	65.0	66.1	68.1	67.4
Hydrogen**	4.7	4.7	4.7	4.6	4.6	4.7	4.7
Nitrogen**	1.6	1.6	1.5	1.6	1.5	1.5	1.6
% Oxygen**	6.7	6.1	6.7	6.9	7.3	6.8	6.4
% Moisture**	2.2	2.0	2.2	2.3	2.4	2.2	1.9
Total	94.15	93.88	95.28	92.83	93.87	94.47	93.63

*Sum of 28 element concentrations in pulverized coal sample (Table 17).
**From ultimate coal analysis (Table 14).

CHARACTERIZATION OF WASTE STREAMS

The characteristics of each trace element in coal cause each element to be dispersed to the various ash streams or to volatilize and be released to the atmosphere in the stack gas following combustion. The primary objective of this effort was to simply characterize the waste streams from a utility boiler.

TABLE 17. CONCENTRATIONS OF TRACE ELEMENTS FOR WHOLE COAL, PULVERIZED COAL, PYRITES, BOTTOM ASH AND MECHANICAL COLLECTOR ASH (μg/g)

TEST	Ag	Al	As	B	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe
WHOLE COAL														
114	<5	24500	19.	76.	174.	1.6	2270	0.14	670.	15.	30	32.	139.	16000
115	10	24500	13.	63.	194.	1.7	1860	0.14	600.	15.	29	30.	145.	14500
117														
119	<5	27500	20.	80.	224.	1.7	1830	0.12	660.	15.	30	30.	154.	17100
120	<5	27000	12.	66.	216.	1.7	1510	0.07	580.	15.	29	27.	157.	12300
121	<5	21500	7.	67.	165.	1.4	2060	0.14	600.	20.	25	24.	146.	13600
122	<5	27000	13.	79.	195.	1.6	1830		940.	25.	34	35.	157.	15600
PULVERIZED COAL														
114	5	25000	13.	76.	199.	1.7	1840	0.20	600.	15.	28	28.	142.	14100
115	20	22500	12.	71.	208.	1.6	1780	0.14	820.	10.	25	26.	148.	14100
117	<5	22500	11.	72.	184.	1.6	1890	0.11	840.	20.	24	26.	142.	13000
119	<5	25000	16.	78.	188.	1.7	1860	0.06	690.	20.	27	26.	148.	15800
120	<5	26000	11.	66.	171.	1.9	1830	0.13	620.	15.	29	27.	151.	11400
121	<5	23000	11.	68.	172.	1.6	2020	0.18	500.	10.	25	23.	131.	13200
122	<5	24000	10.	74.	205.	1.5	2080	0.14	600.	10.	27	25.	145.	15100
PYRITES														
114	10	14500	130.	460.	102.	0.50	12800	0.44	150.	25.	36	30.	68.2	105000
115	10	14500	130.	460.	102.	0.50	12800	0.44	150.	25.	36	30.	68.2	105000
117	10	14500	130.	460.	102.	0.50	12800	0.44	150.	25.	36	30.	68.2	105000
119	10	12500	170.	460.	82.	0.53	10000	0.20	100.	40.	41	30.	61.0	100000
120	10	12500	170.	460.	82.	0.53	10000	0.20	100.	40.	41	30.	61.0	100000
121	10	12500	170.	460.	82.	0.53	10000	0.20	100.	40.	41	30.	61.0	100000
122	10	12500	170.	460.	82.	0.53	10000	0.20	100.	40.	41	30.	61.0	100000
BOTTOM ASH														
114	<5	130000	6.3	232.	867.	7.7	8370	0.06	7.2	70.	154	105.	<10.	93000
115	10	135000	7.0	232.	1060.	8.1	8480	0.41	8.0	70.	145	109.	<10.	95900
117	15	135000	4.3	255.	1050.	7.9	9530	0.28	9.2	75.	144	106.	<10.	101000
119	10	130000	4.0	250.	926.	7.8	8460	0.21	5.2	80.	145	110.	<10.	96700
120	5	130000	7.3	205.	824.	8.2	7030	0.22	26.0	76.	153	111.	<10.	77100
121	<5	130000	4.0	242.	894.	8.1	9660	0.14	4.8	75.	155	108.	<10.	97400
122	5	130000	4.7	251.	1010.	7.6	9460	0.22	5.0	70.	146	110.	<10.	103000
MECHANICAL COLLECTOR														
114	10	125000	48.	244.	929.	9.0	9360	0.21	14.	10.	149	132.	<10.	79800
115	10	120000	43.	235.	1150.	9.2	9930	0.21	19.	25.	146	140.	<10.	89100
117	10	145000	68.	240.	1020.	9.5	10500	0.25	38.	75.	145	143.	<10.	87000
119	10	140000	68.	241.	912.	8.5	9140	0.23	32.	80.	144	123.	<10.	84000
120	10	150000	48.	189.	813.	8.9	6880	0.17	29.	70.	148	124.	<10.	62500
121	25	140000	67.	227.	878.	8.8	10300	0.33	21.	70.	143	128.	23.	80300
122	10	140000	52.	237.	988.	7.8	10500	0.30	17.	85.	142	129.	<10.	86100

TABLE 17. (Continued)

Test	Hg	K	Mg	Mn	Na	Ni	Pb	S	Sb	Se	Si	Ti	V	Zn
WHOLE COAL														
114	0.65	4780	1290	71.0	380.	24.	15.1	24400	1.1	4.8	48100	1410.	49.	25.
115	0.41	5280	1360	40.8	380.	24.	13.8	22700	1.8	4.5	48000	1380.	50.	25.
117														
119	0.27	4930	1380	41.1	480.	20.	16.4	19200	1.4	4.9	55300	1500.	50.	32.
120	0.26	5280	1370	43.9	440.	20.	19.3	18300	1.0	4.8	56100	1460.	47.	28.
121	0.22	3930	1160	34.1	400.	18.	16.7	22200	1.6	4.8	43000	1210.	41.	30.
122	0.30	5360	1550	61.9	460.	36.	17.2	22900	1.4	4.5	54400	1490.	48.	25.
PULVERIZED COAL														
114	0.57	5400	1340	36.3	420.	18.	18.4	22200	0.8	6.9	53400	1580.	50.	27.
115	0.22	4640	1240	33.8	360.	18.	14.3	20400	1.8	5.4	45900	1370.	46.	22.
117	0.26	4080	1220	29.6	380.	18.	16.0	19500	1.5	5.6	42500	1290.	45.	23.
119	0.22	5480	1330	36.4	460.	20.	16.4	19300	3.4	6.9	52200	1490.	48.	27.
120	0.18	5250	1300	32.4	400.	18.	15.6	16500	1.1	7.0	54200	1560.	49.	25.
121	0.18	5200	1140	38.5	380.	17.	16.3	18700	1.0	7.5	45600	1320.	43.	25.
122	0.22	4790	1300	40.8	380.	17.	14.0	20200	1.0	6.8	45800	1390.	49.	21.
PYRITES														
114	0.76	3000	1800	262.	290.	28.	109.	407000	0.8	11.	55600	1300.	57.	63.
115	0.76	3000	1800	262.	290.	28.	109.	407000	0.8	11.	55600	1300.	57.	63.
117	0.76	3000	1800	262.	290.	28.	109.	407000	0.8	11.	55600	1300.	57.	63.
119	0.89	2460	1240	290.	260.	28.	105.	407000	1.2	16.	42600	1000.	58.	59.
120	0.89	2460	1240	291.	260.	28.	105.	407000	1.2	16.	42600	1000.	58.	59.
121	0.89	2460	1240	291.	260.	28.	105.	407000	1.2	16.	42600	1000.	58.	59.
122	0.89	2460	1240	291.	260.	28.	105.	407000	1.2	16.	42600	1000.	58.	59.
BOTTOM ASH														
114	<0.10	20500	6140	223.	1800.	113.	62.3	1780	1.4	2.50	268000	7410.	224.	120.0
115	<0.10	19300	6670	240.	1800.	111.	45.8	1080	1.5	2.00	267000	7260.	231.	43.1
117	<0.10	20500	7100	228.	1900.	122.	37.4	660	1.2	1.70	273000	7330.	229.	65.7
119	<0.10	21500	6620	227.	1800.	104.	50.2	1080	0.9	4.19	278000	7260.	230.	43.0
120	<0.10	21200	6440	217.	1700.	106.	35.7	800	1.3	2.19	289000	7720.	228.	43.2
121	<0.10	21800	6500	307.	1800.	114.	44.8	990	1.7	1.79	280000	7480.	226.	37.9
122	<0.10	19600	6890	259.	1800.	112.	55.9	1030	1.2	1.68	267000	7170.	231.	45.9
MECHANICAL COLLECTOR														
114	<0.10	24300	6770	178.	2000.	111.	72.9	850	1.7	1.70	298000	7780.	268.	94.0
115	0.22	24400	7110	201.	2000.	115.	82.7	800	3.6	1.70	290000	7540.	271.	91.0
117	0.12	20300	7170	181.	2100.	123.	78.5	890	2.4	3.30	279000	7240.	277.	101.0
119	<0.10	22100	6860	191.	1900.	108.	67.8	890	2.4	2.20	291000	7260.	273.	99.8
120	<0.10	21600	6770	172.	1800.	106.	75.4	890	3.1	2.80	300000	7560.	253.	100.0
121	0.10	19400	6780	226.	2000.	105.	69.5	800	3.2	3.30	283000	7280.	255.	131.0
122	0.15	18500	6900	200.	2100.	106.	75.9	1170	2.2	3.30	269000	7020.	241.	92.0

Coal and Ash

The concentration of a number of trace elements was investigated in each of the daily test samples of pulverized coal, pyrites, and the ash samples. The results are reported in Tables 17 and 18. As one might anticipate, the major constituents of the ash were iron, aluminum, and silicon. Following these three major constituents in order of abundance in the ash samples were potassium, calcium, sodium, magnesium, sulfur, and titanium.

Ash Sluice Water

To provide background water quality data, inflow water samples were collected during each daily test. All bottom ash samples and eight ESP fly ash samples were collected as slurry as they were being sluiced to the ash pond. Following the 14-hour settling period, all the water was siphoned from the settled solids, the decanted water volume was measured, and a sample was retained for analysis. Results of the field and laboratory water analyses are reported in Tables 3, 19, and 20.

This sampling scheme was used to evaluate the leaching characteristics of the major and minor trace elements in ash. Bottom ash had little effect on the raw sluice water trace element concentration (Tables 19 and 20). During the bottom ash sluicing, Ba, Mn, and Si appeared to have been partially removed from the dissolved portion of the sluice water during the ash sluicing. The effect of ESP ash (Tables 19 and 20) on the raw sluice water dissolved trace elements was generally greater than the effect of the bottom ash. Constituents showing the largest increases were Al, As, Ba, B, Cu, Si, and Fe. Sb, Ca, Cd, Cr, Mn, Ni, K, and Se showed slight increases. This increase is expected because of the higher surface area of the fly ash.

Fine Particulate Characterization

It should be noted that variables exist, inherent to impactor operation, which degrade the data somewhat under any circumstances. A large magnitude of particles flowing through an impactor do not land on any stages, but adhere to available surfaces (such as the nozzle, the cone, the impactor plates). It had been suggested at the time of these tests that particles lost above the first stage be included in the first stage's weight. In fact, later calibration studies have indicated that these particles do not belong there. However, the question of how to account for this loss quantitatively can not be settled without sophisticated impactor calibrations.

Any poor laboratory and impactor handling technique will tend to bias or distort the actual distribution. For instance, if the impactor head is struck during transport after sampling, dust from one stage can be knocked to a lower stage. This effect is more pronounced at the lower stages where only a few large particles can dramatically increase the weight of a submicron particle stage. By the same token, any loss of tare weight (torn filters) can have a sizable effect on the weight distribution.

TABLE 18. CONCENTRATIONS OF TRACE ELEMENTS FOR RC ESP INLET, RC ESP HOPPER, AAF ESP INLET, AAF ESP HOPPER, AND AAF ESP OUTLET (μg/g)

TEST	Ag	Al	As	B	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe
							RC ESP INLET							
114		85400	59.6	314.	552.	8.6	9350	12.7	3720.	75.6	1420	166.	357.	56900
115		98400	84.5	239.	850.	9.3	12300	8.1	1500.	47.7	589	179.	191.	57400
117		78200	118.	389.	400.	10.2	4790	29.0	14400.	80.2	1320	187.	201.	60600
119		84100	94.3	325.	510.	8.6	6430	27.8	6570.	58.6	849	142.	372.	51400
120		85300	53.	310.	373.	9.5	4970	20.0	4800.	57.5	488	144.	375.	42600
121		82800	61.4	316.	521.	9.8	4530	9.6	3390.	58.7	730	156.	326.	51900
122		82100	60.7	315.	558.	8.4	3530	14.3	4080.	65.1	1770	161.	510.	58000
							RC ESP HOPPER							
114	15	140000	130.	228.	1020.	10.9	9610	1.7	7.0	55.	160	198.	69.1	64400
115	10	140000	120.	283.	1000.	10.5	9750	1.4	5.2	60.	154	167.	41.	72200
117	15	140000	93.	260.	1070.	11.3	10800	2.1	7.4	55.	172	209.	114.	67700
119	10	140000	140.	302.	950.	10.0	9000	1.6	46.0	50.	155	182.	87.2	63900
120	10	145000	100.	277.	860.	10.2	7850	1.4	8.6	65.	153	180.	87.2	55800
121	10	140000	140.	273.	940.	10.9	8950	2.0	9.8	50.	157	180.	115.	57100
122	10	140000	140.	258.	1020.	10.0	10200	2.3	5.4	55.	155	184.	156.	60600
							AAF ESP INLET							
114		104000	123.	264.	1280.	8.93	7890	16.4	528.	58.7	1330	285.	1160.	75300
115		98500	8.4	84.2	1300.	8.96	8110	32.6	960.	60.2	1150	287.	985.	53000
117		95200	134.	157.	1360.	9.55	9360	58.3	97.1	95.1	3550	480.	577.	65000
119		106000	116.	220.	1190.	8.66	10700	38.5	1380.	71.5	2260	281.	494.	64700
120		108000	107.	308.	1130.	10.30	11500	15.2	942.	106.	2030	232.	925.	52000
121		111000	143.	119.	1420.	10.90	11200	16.4	1680.	63.3	751	219.	1990.	50400
122		112000	31.5	204.	1530.	9.52	12900	56.3	112.	64.8	1450	217.	195.	63100
							AAF ESP HOPPER							
114	10	145000	170.	312.	855.	10.1	7880	3.3	8.6	65.	167	190.	179.	57700
115	55	145000	220.	326.	1010.	11.0	9750	4.1	8.6	60.	184	222.	286.	59400
117	25	145000	190.	349.	1070.	10.8	11600	3.9	8.6	65.	183	220.	209.	62700
119	15	140000	180.	359.	1000.	10.0	9740	4.5	11.0	60.	171	198.	199.	59400
120	10	145000	170.	326.	970.	11.7	9200	3.7	13.0	65.	178	198.	369.	55200
121	15	140000	170.	364.	1020.	12.1	9850	5.7	13.0	65.	196	214.	533.	57300
122	15	145000	190.	324.	1120.	10.8	11000	4.2	8.6	65.	186	210.	160.	60600
							AAF ESP OUTLET							
114		7200	13.6	1640.	88.2	1.83	4960	838.		305.	49100	623.		181000
115		7570	26.7	<225.	74.6	<1.18	6530	1080.	<8210.	<135.	15300	330.	<956.	70600
117		4820	116.	48.8	31.6	0.26	2800	407.	<4160.	30.2	3250	104.	<375.	32600
119		9270	109.	<109.	55.5	0.06	6270	2970.		<69.8	6810	445.		34700
120														
121		6500	<2.6	<12.2	<11.1	<0.28	1470	496.	546.	10.3	<650	13.7	185.	3290
122									1190.				<1180.	

TABLE 18. (Continued)

Test	Hg	K	Mg	Mn	Na	Ni	Pb	S	Sb	Se	Si	Ti	V	Zn
						RC ESP INLET								
114	0.36	14500	6710	283.	1440.	1230.	70.3	6280	6.1	<0.72		5940.	206.	213.
115	0.35	15800	8460	201.	9390.	505.	77.9	5800	4.7	<0.50		6880.	271.	234.
117	0.22	11200	3040	268.	5830.	1300.	66.4	7890	6.3	<3.72		6930.	288.	217.
119	0.46	14500	4750	183.	10900.	785.	70.9	5150	5.5	<0.64		6530.	238.	218.
120	0.64	13000	4010	153.	9660.	478.	65.1	3930	4.3	<0.50		6940.	240.	225.
121	1.26	13200	6140	226.	8850.	683.	70.7	5260	5.5	<0.74		7030.	263.	220.
122	0.26	14500	6260	264.	8970.	1400.	67.6		4.4	<0.55		6260.	308.	224.
						RC ESP HOPPER								
114	0.18	21700	7500	207.	2300.	132.	103.	2390	3.3	6.0	230000	7400.	313.	212.
115	0.20	17300	7600	210.	2400.	141.	122.	2720	4.2	5.5	227000	7550.	298.	244.
117	0.15	21800	7900	221.	2400.	137.	111.	2300	4.6	8.8	229000	7540.	329.	244.
119	0.22	20200	7900	203.	2500.	121.	135.	2630	3.3	8.5	236000	7350.	296.	228.
120	0.20	22500	7700	190.	2200.	129.	110.	2110	2.3	10.0	248000	7400.	293.	239.
121	0.23	24400	7850	240.	2600.	126.	116.	2720	3.3	10.0	254000	7650.	291.	208.
122	0.23	23500	7900	240.	2600.	128.	110.	2540	2.2	9.7	243000	7550.	296.	205.
						AAF ESP INLET								
114	0.98	18600	7460	352.	12400.	913.	104.		8.	29.1		6060.	274.	476.
115	0.20	17000	3530	281.	2780.	620.	107.		7.5	27.3		5730.	283.	602.
117	0.25	17300	6790	514.	2810.	2400.	130.		8.3	23.4		5810.	299.	1030.
119	0.45	19900	8020	488.	2270.	1800.	118.		7.4	<10.8		5850.	269.	594.
120	0.20	17900	9220	414.	2070.	1230.	111.		5.8	19.2		6390.	290.	673.
121	0.22	19800	8240	295.	3420.	499.	129.		11.1	11.6		6370.	318.	496.
122	0.29	21800	9070	394.	3730.	993.	93.6		4.1	7.25		6430.	276.	347.
						AAF ESP HOPPER								
114	0.22	23100	7150	182.	2400.	140.	125.	3690	6.	14.	247000	7500.	316.	261.
115	0.12	20200	7550	214.	2600.	160.	128.	4200	6.	17.	228000	7480.	349.	302.
117	0. 5	21300	8050	230.	2800.	163.	136.	3640	4.6	16.	226000	7500.	348.	298.
119	0.10	19100	8150	224.	2800.	145.		4200	6.2	16.	230000	7360.	323.	403.
120	0.10	19700	8180	232.	2500.	153.	132.	5850	5.8	15.	229000	7660.	335.	328.
121	0.15	20100	8150	250.	2600.	161.	169.	7350	7.1	22.	234000	7730.	365.	368.
122	0.15	22200	8400	257.	2800.	152.	139.	4670	5.2	16.	222000	8040.	334.	490.
						AAF ESP OUTLET								
114	0.80	1990	2180	4060.	6790.	16400.	37.4		<5.1	<185.0		391.	151.	<2500.
115	<0.25	2160	2590	1360.	23400.	6350.	<45.4		5.6	35.0		322.	62.6	<2560.
117	2.62	2020	1560	<402.	25600.	1590.	<67.4		<5.5	<25.9		203.	20.1	<1770.
119	4.92	2340	3280	<655.	35900.	3560.	56.		<2.7	123.0		310.	38.7	511.
120														
121	<0.10	336	619	70.6	9520.	1160.	17.2		<5.8	<4.17		<32.8	<3.4	534.
122														

TABLE 19. TRACE ELEMENT CONCENTRATIONS IN INFLOW WATER SAMPLES (μg/ℓ) EXCEPT AS NOTED

Test	Al	Sb	As	Ba	Be	B	Ca[1]	Cd	Cl[1]	Cr	Co	Cu	F[1]	Fe	Pb	Mg[2]	Mn	Hg	Ni	K[1]	Se	Si	Ag	Na[1]	SO_4[1]	Tl	Ti	V	Zn
Inflow Water (Suspended)																													
114	370	<2	<2	34	<.5	<5	28	<1	2	<5	<5	43	0.04	730	<10	6.4	58	0.3	9	1.7	<1	2100	<10	2.8	17	<50	5	6	54
115	390	<2	<2	34	<.5	<5	29	<1	2	<5	<5	59	0.03	600	<10	6.5	60	1.7	<5	1.6	<1	2100	<10	2.3	17	<50	4	<5	270
117	460	<2	<2	34	<.5	<5	27	<1	3	<5	<5	62	0.02	900	<10	6.4	74	<.2	<5	1.6	<1	2100	<10	2.5	17	<50	4	<5	37
119	520	<2	<2	36	<.5	<5	29	<1	3	<5	<5	64	0.03	1000	<10	6.4	97	<.2	<5	1.9	<1	2000	<10	2.7	18	<50	5	<5	140
120	430	<2	<2	38	<.5	<5	28	<1	3	<5	<5	39	0.02	730	<10	6.6	68	<.2	<5	1.7	<1	2300	<10	3.0	17	<50	6	<5	52
121	470	<2	<2	38	<.5	<5	28	<1	2	<5	<5	80	0.02	1300	<10	6.5	76	<.2	6	1.6	<1	2000	<10	2.9	18	<50	6	<5	33
122	410	<2	<2	38	<.5	<5	29	<1	2	<5	<5	51	0.04	780	<10	6.5	66	<.2	<5	1.8	<1	2300	<10	3.0	18	<50	4	<5	95
Inflow Water (Dissolved)																													
114	90	<2	6	55	1.3	<5	27	<1	3	<5	<5	<5	<0.10	7	<10	6.4	24	0.2	6	1.6	<1	2200	<10	3.5	18	<50	2	<5	<2
115	100	<2	2	61	0.7	11	29	<1	3	<5	<5	<5	<0.10	<5	<10	6.7	24	<.2	<5	1.7	<1	2300	<10	3.2	15	<50	<1	<5	<2
117	80	<2	6	53	0.7	<5	29	<1	3	<5	<5	<5	<0.10	<5	<10	6.6	23	<.2	<5	1.8	<1	2300	<10	3.3	20	<50	<1	<5	<2
119	100	<2	2	64	0.6	<5	30	<1	3	<5	<5	<5	<0.10	9	<10	6.7	27	<.2	5	1.8	<1	2300	<10	3.2	21	<50	<1	<5	<2
120	130	<2	4	69	0.6	<5	40	<1	3	<5	<5	<5	<0.10	82	<10	6.8	30	<.2	7	1.8	<1	2300	<10	3.5	18	<50	<1	<5	120*
121	70	<2	4	60	<.5	5	31	<1	3	<5	<5	8	<0.10	<5	<10	6.9	28	<.2	5	1.7	<1	2500	<10	3.6	24	<50	<1	<5	<2
122	100	<2	5	54	<.5	<5	31	<1	3	<5	<5	<5	<0.10	<5	<10	6.8	20	0.5	6	1.6	<1	2400	<10	3.5	20	<50	<1	<5	<2

*Value questionable

[1] Units for these elements are mg/ℓ.

TABLE 20. TRACE ELEMENT CONCENTRATIONS IN BOTTOM ASH AND ELECTROSTATIC PRECIPITATOR SLUICE WATER SAMPLE (μg/ℓ) EXCEPT AS NOTED

Test	Al	Sb	As	Ba	Be	B	Ca[1]	Cd	Cl[1]	Cr	Co	Cu	F[1]	Fe	Pb	Mg[1]	Mn	Hg	Ni	K[1]	Se	Si	Ag	Na[1]	SO_4[1]	Tl	Ti	V	Zn
Bottom Ash Sluice Water (Dissolved) Setting Time 14 h																													
114	70	<2	<2	30	<.5	<5	27	<1	2	<5	<5	34	<0.1	31	<10	6.5	<5	<.2	<5	1.5	<1	1900	<10	2.6	17	<50	2	<5	4
115	50	<2	<2	29	<.5	<5	28	<1	2	<5	<5	57	<0.1	31	<10	6.6	<5	.2	<5	1.5	<1	2000	<10	2.5	23	<50	2	<5	18
117	70	<2	<2	28	<.5	<5	28	<1	2	<5	<5	27	<0.1	20	<10	6.6	<5	<.2	<5	1.5	<1	2000	<10	2.4	16	<50	2	<5	28
119	50	<2	<2	28	<.5	<5	27	<1	3	<5	<5	30	<0.1	17	<10	6.5	<5	<.2	<5	1.5	<1	2000	<10	2.3	16	<50	2	<5	23
120	50	<2	<2	28	<.5	<5	30	<1	2	<5	<5	49	<0.1	64	<10	6.6	6	<.2	<5	1.6	<1	2100	<10	3.2	16	<50	2	<5	42
121	170	<2	<2	30	<.5	<5	29	<1	2	<5	<5	78	<0.1	130	<10	6.6	7	<.2	<5	1.5	<1	2000	<10	2.5	10	<50	3	<5	42
122	90	<2	<2	29	<.5	<5	27	<1	2	<5	<5	36	<0.1	52	<10	6.4	<5	<.2	<5	1.5	<1	2000	<10	2.5	17	<50	3	<5	<2
Electrostatic Precipitator Sluice Water (Dissolved) Settling Time 14 h																													
114	940	3	270	140	<.5	390	44	<1	-	15	<5	60	-	17	<10	6.5	7	-	<5	5.4	6	2200	<10	3.5	-	<50	2	46	<2
115	180	13	80	310	1.7	1500	73	8	-	15	10	100	-	36	<10	8.8	60	-	38	16	12	3800	<10	9.4	-	<50	4	30	30
117	250	15	42	340	0.5	1000	62	5	-	17	9	34	-	91	<10	8.7	44	-	33	12	12	3300	<10	6.9	-	<50	11	40	<2
119	80	8	130	320	<.5	980	60	5	-	11	8	36	-	68	<10	8.5	49	-	30	11	14	3200	<10	6.5	-	<50	3	34	<2
120	2700	6	200	380	1.9	720	58	9	-	44	11	170	-	410	<10	8.9	96	-	38	11	6	2800	<10	7.5	-	<50	4	14	220
121	5500	10	60	370	2.7	720	46	11	-	38	14	260	-	520	<10	8.2	95	-	46	12	2	2900	<10	8.0	-	<50	4	9	73
122	3600	13	75	330	1.9	650	46	9	-	13	12	180	-	590	<10	8.1	88	-	40	11	4	2700	<10	6.5	-	<50	9	16	76

[1] Units for those elements are mg/ℓ.

Taking into account the care needed in sampling and laboratory handling techniques, it is not uncommon to observe as many "poor" runs as "good" quality runs.

Brinks - Inlet to RC ESP

The Brinks data, gathered at the inlet to old ESP's, have been both manually plotted and averaged by computer techniques. Because the scatter in the data was quite large, no meaningful results were obtained. It was clear that these runs had problems beyond normal operating problems of impactors.

Brinks - Outlet to RC ESP (Inlet to AAF ESP's)

The Brinks was run at this location in the hopes that it would provide a check on the Andersen results. Unfortunately, the flow conditions at this location did not lend themselves to Brink operating conditions. The Brink is a low-flow impactor and isokinetic sampling conditions were impossible to achieve with the high velocity of flue gas existing at this location.

The Brinks data has been hand-plotted and the results only substantiate the sampling problems. Therefore, no meaningful analysis can be applied to this set of data.

Andersen - AAF ESP Outlet

The tests performed at the new ESP outlet were all invalidated due to two primary effects: the dust loading was so light at this location, supported by total particulate tests, that inordinate sampling durations were necessary to collect a gravimetric sample; unfortunately, the long sample times allowed a substantial amount of sulfur weight gain on the filters which overshadowed the particulate weight gain.

This problem was dealt with by conditioning the filters with flue gas prior to actual sampling. Unfortunately, a consistent weight gain vs time or volume of gas conditioned could not be charted. It was only after this field study that a laboratory procedure for conditioning substrates was developed and distributed in an EPA manual.

In effect, no meaningful impactor data was collected at the new ESP outlet.

Andersen - Outlet to RC ESP (Inlet to AAF ESP)

Particle size distributions were fitted to a log-normal distribution from data gathered at the Kingston Steam Plant using a Mark III, Andersen 2000 impactor. At first, graph diameters based on standardized operating conditions were used, but the results were not acceptable. The diameters were calculated based on stage calibration constants and other operating parameters and the data again fit to the log-normal distribution. Examination of experimental conditions identified abnormal runs. The "good" runs were satisfactorily fitted to the log-normal distribution using both graph and calculated diameters. The geometric mean as estimated using the graph diameters was 5.16 microns and using the calculated diameters was 4.39 microns. Table 21 shows the sampling parameters for each run.

Fitting Particle Size Distributions

Impactor data gathered downstream from electrostatic precipitators was analyzed for the purpose of estimating the aerodynamic mean of the particulate diameters. The results provided particle size distribution information used in design requirements for electrostatic fly ash collectors, flue gas desulfurization systems, and baghouse collectors. All statistical results pertain to the operating conditions, equipment configuration, and experimental conditions in effect at the Kingston Steam Plant during the period of the study.

The distribution of particle diameters versus the percentage less than the stated size was assumed to be log-normal. This assumption was checked for all runs using the Kolmogorov-Smirnov test of goodness of fit.[1] Two techniques were initially used to estimate the particle diameters: (1) based on the actual sample flow, a particle diameter was estimated from a graph based on Mark III, Andersen 2000 impactors, standardized to 300°F air temperature; and (2) based on stage calibration constants, gas viscosity, jet velocity, the Cunningham slip correction factor and other operating variables, the particle diameters were calculated. The calculated diameters technique was adopted as the standard because of its increased accuracy and responsiveness to operating conditions. Least squares estimation of the distribution function was checked for adequacy by standard techniques such as the F ratio, R^2, and residual plots analysis. Based on these and other criteria, outliers in the field data were identified. Subsequent investigation revealed that, for the outliers, aberrations had occurred in the experimental conditions. After examination of all the above criteria, the resulting estimates of the geometric particle diameter mean were accepted as being reasonable and valid.

Explanation of F-Ratio, R^2, Regression Residuals, and Error Mean Square

The F-value, or F-ratio, tests how well the log-normal distribution as a whole (after adjusting for the mean) accounts for the behavior of the particle size diameter (dependent variable).

R^2 measures how much of the dependent variable's variation can be explained by the log-normal distribution. R^2 can range from 0 to 1 and, in general, the larger the value of R^2, the better the log-normal distribution's fit.

Residuals are the difference between the actual diameter noted and the diameter predicted by the fitted log-normal distribution. As such, the residuals will reflect any systematic deviation in the data from the distribution fitted. Plots of residuals are commonly used to identify shortcomings in the hypothesized model being fitted.

TABLE 21. ANDERSEN IMPACTOR SAMPLING PARAMETERS - INLET AFF ESP

Run No.	Date	Sample Time	Stack Temp.	Barometric Pressure (in. Hg)	Stack Pressure (in H_2O)	Sample Volume (ft^3)	Sample Flow (acfm)	Nozzle Diam.	Probe Depth	Grain Loadings (From T. Part.)
214-A	7/19/77	16 min.	320°F	29.525	0.55	7.43	0.67	3/16 in.	14 in.	0.2151
215-A	7/20/77	16 min.	320°F	29.52	0.95	7.60	0.69	3/16 in.	14 in.	0.1477
216-A	7/21/77	20 min.	339°F	29.49	0.57	9.03	0.69	3/16 in.	14 in.	0.1466
217-A1	7/22/77	25 min.	325°F	29.44	0.92	10.60	0.63	3/16 in.	44 in.	0.1338
217-A2	7/22/77	25 min.	325°F	29.47	0.92	10.10	0.61	3/16 in.	44 in.	0.1338
219-A1	7/25/77	20 min.	325°F	29.35	1.05	8.62	0.65	3/16 in.	44 in.	0.2910
219-A2	7/25/77	15 min.	325°F	29.35	1.05	6.54	0.66	3/16 in.	44 in.	0.2910
220-A1	7/26/77	15 min.	320°F	29.42	0.92	6.74	0.68	3/16 in.	44 in.	0.0650
220-A2	7/26/77	15 min.	320°F	29.42	1.01	7.37	0.72	3/16 in.	44 in.	0.0650
221-A1	7/27/77	18 min.	320°F	29.46	1.60	8.78	0.75	3/16 in.	44 in.	-
221-A2	7/27/77	18 min.	320°F	29.46	1.60	9.04	0.74	3/16 in.	44 in.	-

"Error mean square" is the variance of the dependent variable as estimated by the residual sum of squares divided by the appropriate degrees of freedom. The closer to the natural random variation in the dependent variable that the error mean square can get, the larger the confidence that an appropriate distribution or model has been specified.

When evaluating a regression analysis, all of the above factors must be considered in total, as any particular one taken alone can sometimes be misleading.

Fitting Size Distributions to Graph Diameters

Eleven runs of particle size distributions, where the diameters were estimated from the Mark III, Andersen 2000 impactor graph previously discussed, were fitted by least squares to a log-normal distribution individually and combined. The regression analysis was of the natural logarithm of the diameters versus the calculated t value of the standardized empirical cumulative distribution of the percent of weights less than the stated size. The geometric particle diameter mean was estimated by setting t=0 and taking the anti-logarithm of the intercept. The calculated F value for the fit is 470.66 with (1,86) degrees of freedom with an associated error mean square of 0.1873. The amount of variation explained by the least squares line as indicated by R^2 x 100 is 85 percent. Examination of the residuals did not indicate any serious model defects or errors in assumptions. Examination of Figures 5 and 6 indicated large run-to-run variation and the possibility that the log-normal distribution might not be appropriate. The Kolmogorov-Smirnov test applied to the combined group indicated significant departure from the log-normal distribution. The individual runs were then examined in order to identify possible aberrations in particular runs. The Kolmogorov-Smirnov test for goodness of fit applied to the individual runs indicated that 9 of the 11 runs were adequately explained by the log-normal distribution (see Table 22). Those runs not corresponding to the log-normal were noted for further examination. It was decided to calculate the particle size diameters based on actual operating parameters and to compare the results with the estimates based on graph diameters to see if a reduction in the run-to-run variation or an improvement to fitting the log-normal distribution occurred.

Fitting Size Distributions to Calculated Diameters

The same eleven runs previously analyzed using graph diameters were analyzed using calculated particle size diameters based on actual operating parameters. The data was fitted individually and collectively to the log-normal distribution. Figure 7 shows the individual fits and Figure 8 shows the group fit for all 11 runs. The calculated F value for the fit is 430.01 with (1,86) degrees of freedom and an associated error mean square term of 0.2273. The amount of variation explained by the least squares line as indicated by R^2 x 100 was 83 percent. Examination of the residuals did not indicate any serious model defects or errors in assumptions.

TABLE 22. GOODNESS OF FIT TEST OF GRAPH DIAMETERS TO THE LOG-NORMAL DISTRIBUTION

Run No.	Maximum Difference	N	Significance Level	Tabled Value*
1	0.156	8	NS**	
2	0.423	8	.10	0.411
3	0.189	8	NS	
4	0.286	8	NS	
5	0.320	8	NS	
6	0.211	8	NS	
7	0.303	8	NS	
8	0.241	8	NS	
9	0.630	8	.01	0.543
10	0.351	8	NS	
11	0.201	8	NS	
All 11 runs combined	1.211	11	.01	0.468

*See Reference No. 1.
**Not significant.

Comparing Figures 5, 6, 7, and 8 in conjunction with the statistics from the least squares, fits did not show any significant statistical benefit from using calculated diameters instead of graph diameters. In fact, there was a moderate (but not significant) loss in the error mean square and the coefficient of determination. Table 23 summarizes the goodness of fit tests on the individual and grouped, calculated particle size diameters. Only runs 3, 6, 7, and 11 seem to follow the log-normal distribution; runs 1, 4, 5, and 8 are marginal.

At this point, the individual runs were examined in depth for the test conditions and experimental results. It was found that the variation in test runs could be attributed to significant aberrations which occurred during experimental runs such as filter overloading or underloading. Only runs 3, 7, 8, and 11 were apparently run without difficulty, substantiating what the goodness of fit tests indicated.

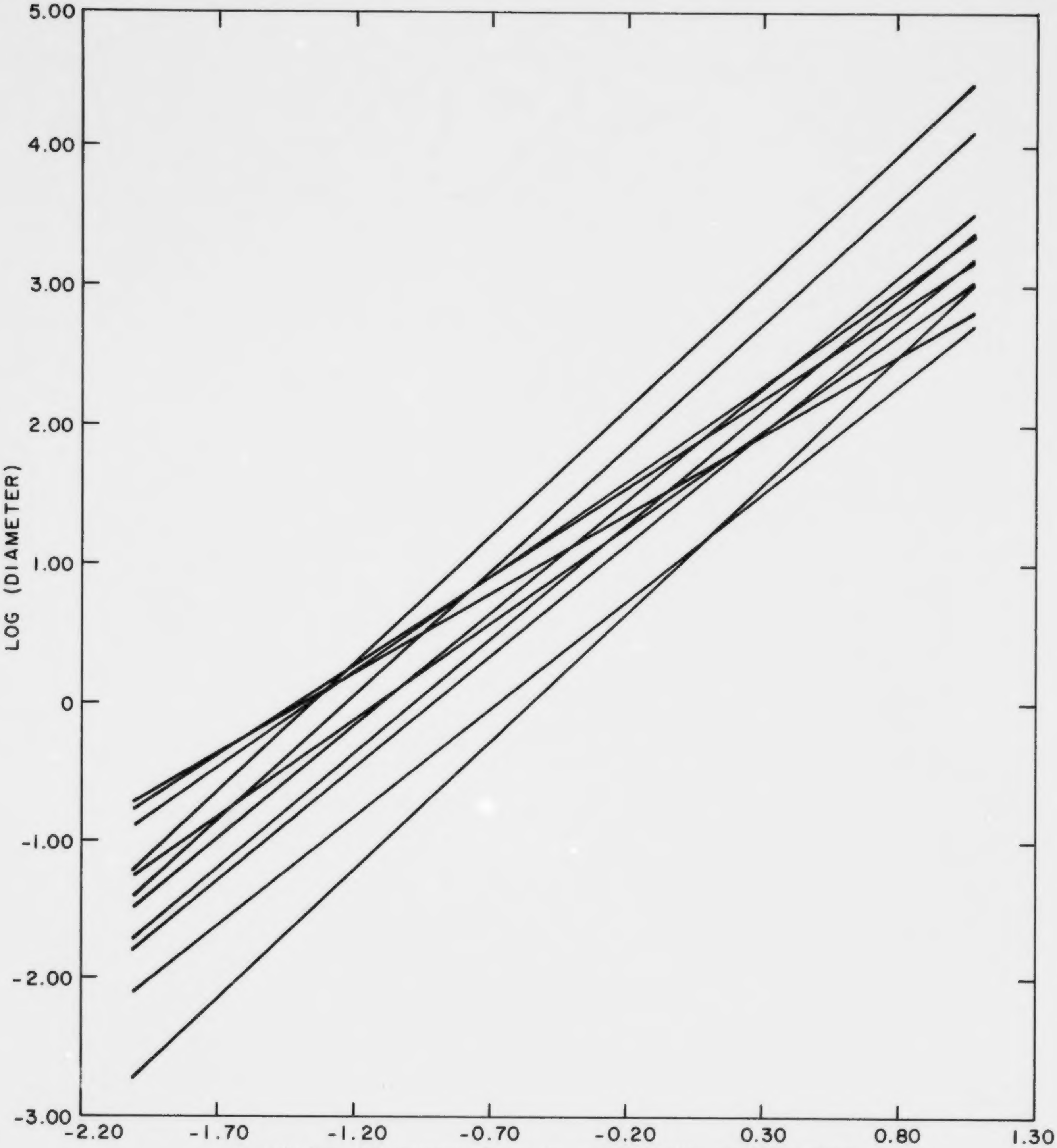


Figure 5. Individual particle size distributions (based on graph diameters) least squares fits to all 11 runs

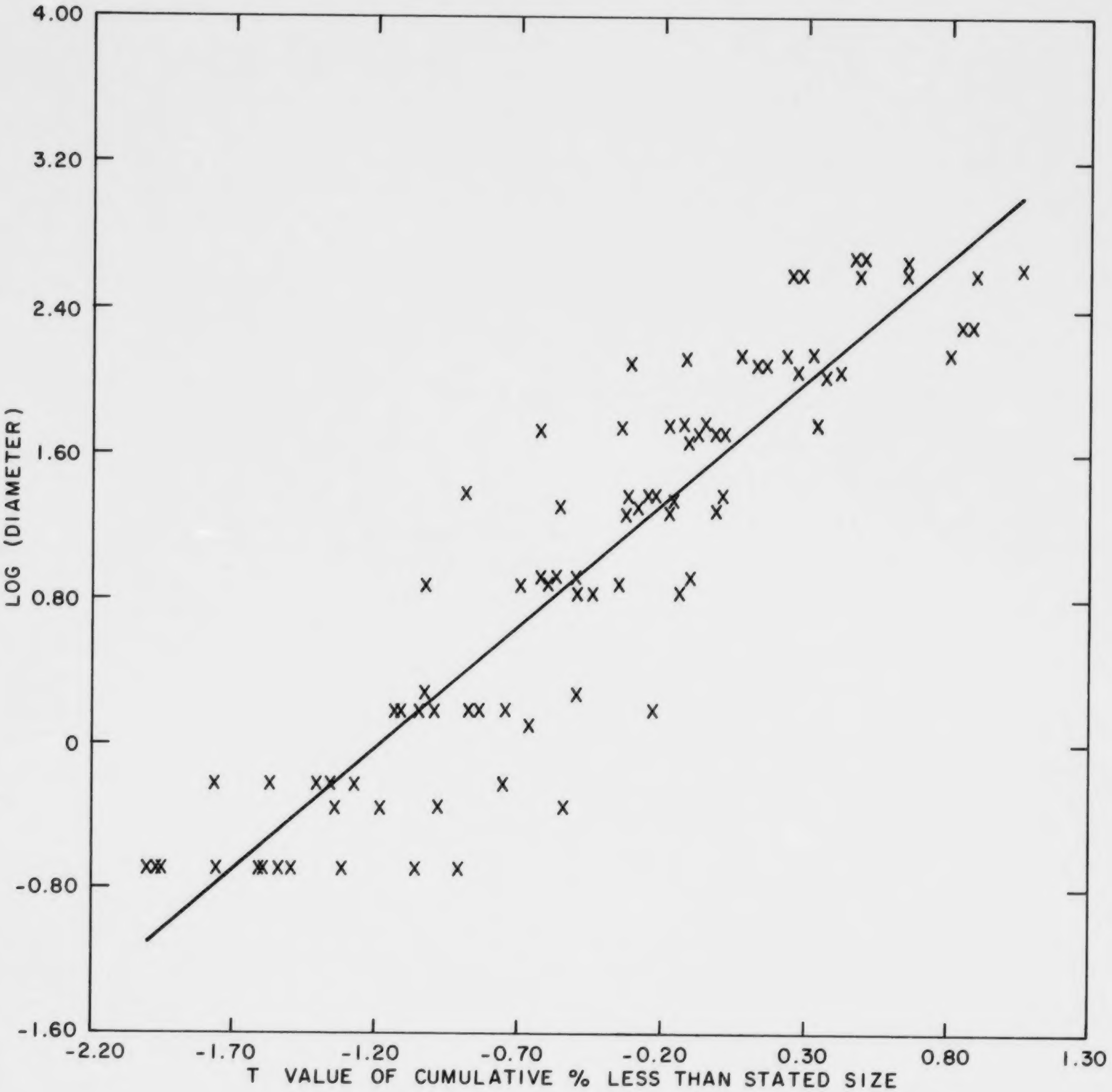


Figure 6. Particle size distribution (based on graph diameters) least squares fit vs. observed values - all 11 runs

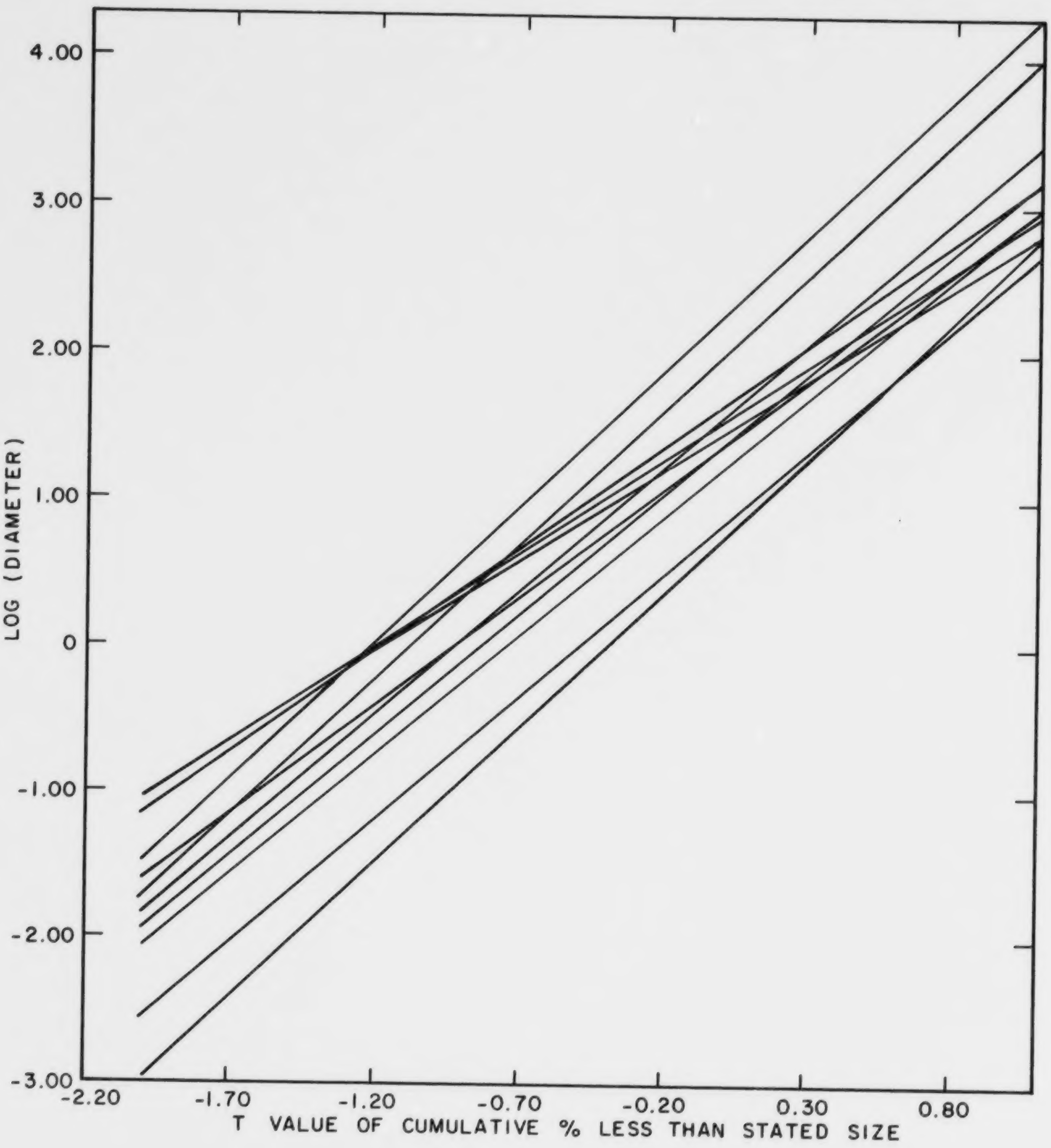


Figure 7. Individual particle size distributions (based on calculated diameters) least squares fits to all 11 runs

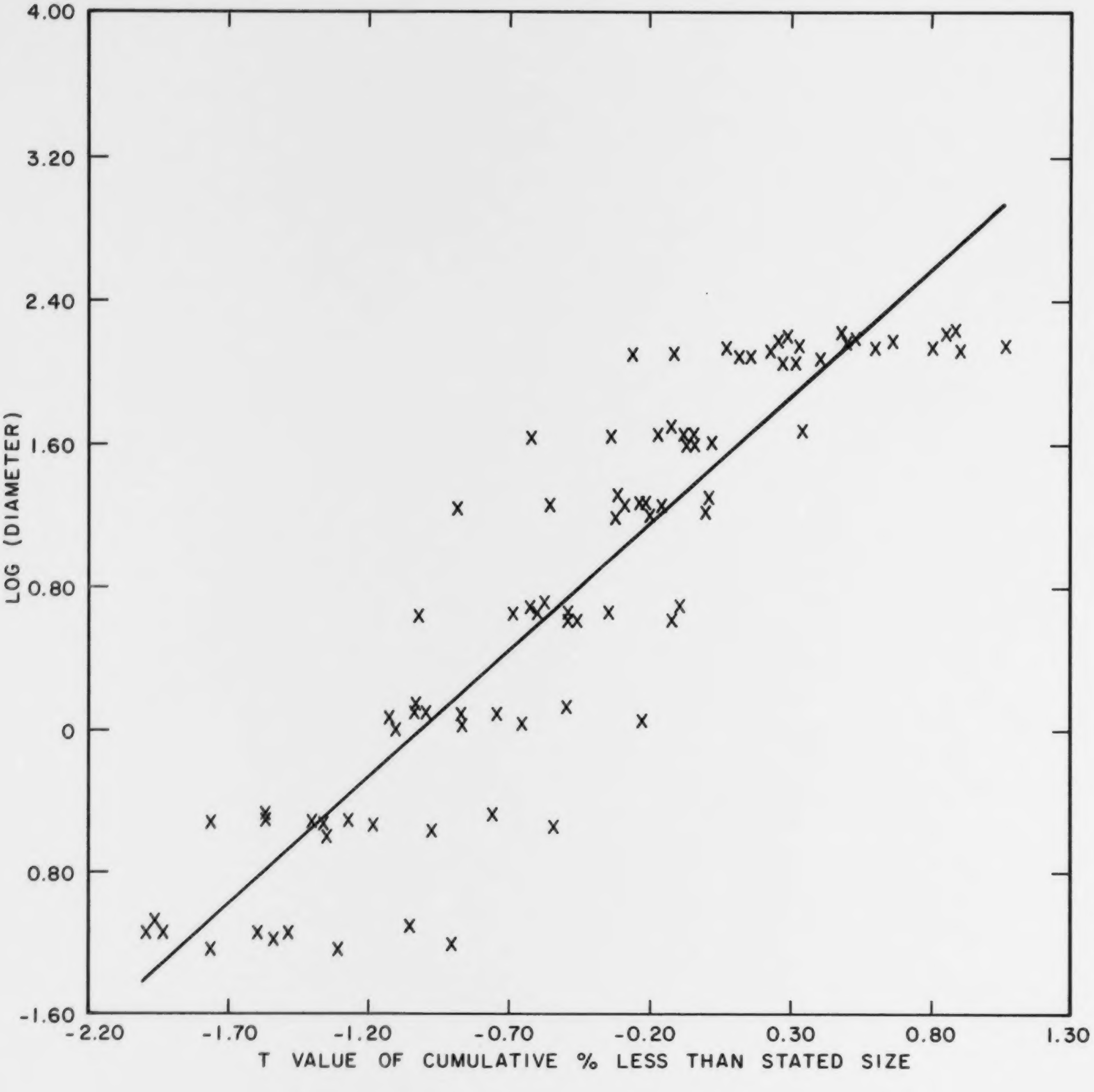


Figure 8. Particle size distribution (based on calculated diameters) least squares fit vs. observed values - all 11 runs

TABLE 23. GOODNESS OF FIT TEST OF CALCULATED DIAMETERS TO THE LOG-NORMAL DISTRIBUTION

Run No.	Maximum Difference	N	Significance Level	Tabled Value*
1	0.415	8	.10	0.411
2	0.649	8	.01	0.543
3	0.327	8	NS**	
4	0.370	8	.20	0.358
5	0.410	8	.15	0.381
6	0.287	8	NS	
7	0.274	8	NS	
8	0.422	8	.10	0.411
9	0.742	8	.01	0.543
10	0.646	8	.01	0.543
11	0.218	8	NS	
All 11 runs combined	1.338	11	.01	0.468

*See Reference No. 1.
**Not significant.

Fitting Size Distributions to Four Selected Runs

The four runs which were identified as not having experimental abberations were runs 3, 7, 8, and 11. These four runs were fitted as a group to the log-normal distributions. The calculated F value was 648.74 with (1,30) degrees of freedom. The error mean square term was 0.0630. The amount of variation explained was 96 percent. Examination of the residuals did indicate one substantially abnormal point. Subsequent investigation did not identify the point as being the result of a coding or clerical error, and remained in the analysis. Except for this one point, the log-normal fit was excellent. Figure 9 illustrates the fit and the data points. Figure 10 shows the group fits using the graph diameters, and Figure 11 compares the group fits using the graph and calculated diameters. Comparisons of these figures indicate there is little difference between using the graph and calculated diameters. Use of the graph diameters resulted in a geometric mean of an estimated 5.16 microns, which is higher than the geometric mean of 4.39 microns estimated by the calculated diameter fit.

CHEMICAL CHARACTERIZATION OF FINE PARTICULATE

Samples from the Andersen Impactor were chemically analyzed in three size fractions. These size fractions were <1 μm, 1 to 3 μm, and >3 μm. Table 24 gives the results from the fine particulate chemical analysis.

Previous studies[2] indicate that Fe and Al are generally predominate in larger particle sizes; Pb, Sb, Se, Hg, and Zn are concentrated in the smaller particle sizes; and the other elements show either no preference to size or are placed in either category depending on which paper is being reviewed.

After a visual observation of the study results (presented in Table 24), it can only be concluded that chemical analysis of such samples is quite difficult and lead to results with a large amount of scatter (orders of magnitude). Error can be introduced at any number of points--sample collection, sample weighing, incomplete recovery of small samples during the preparation for chemical analysis, contamination of samples during physical handling or by the collection substrate, use of two different microchemical analytical techniques, small samples near the limit of sensitivity of the instrument, or during the analysis of the blanks.

The large amount of scatter, due to all of the possible sources of error in dealing with extremely small samples, prevents firm conclusions regarding much of the chemical analysis data. There are, however, some trends that might be pointed out for the reader's consideration. The elements Al, Fe, Mn, Ni, and Se generally had higher concentration in the larger particle ranges, while Na and Ca had higher concentration in the lower ranges.

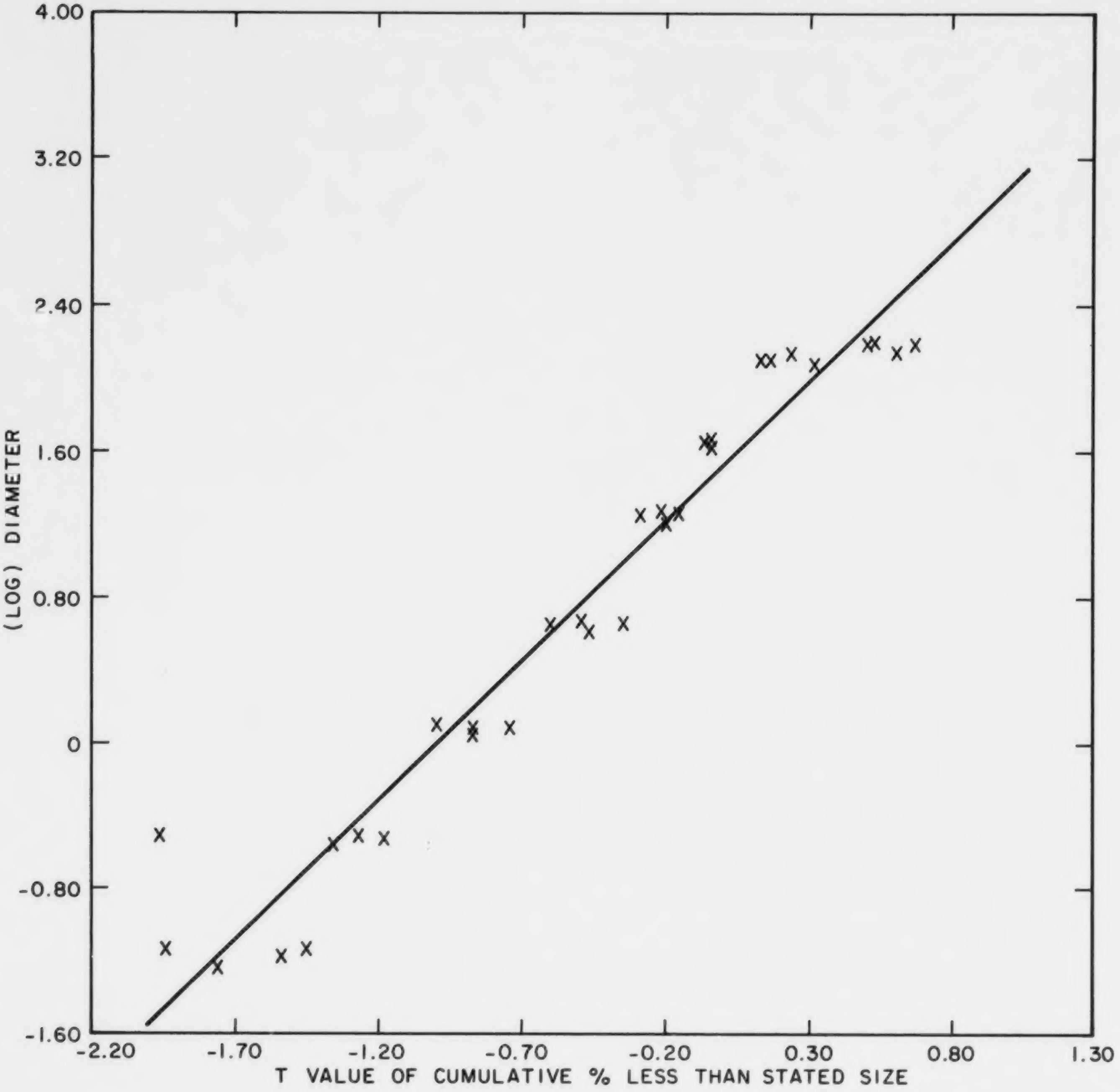


Figure 9. Particle size distribution (based on calculated diameters) least squares fit vs. observed values - 4 selected runs

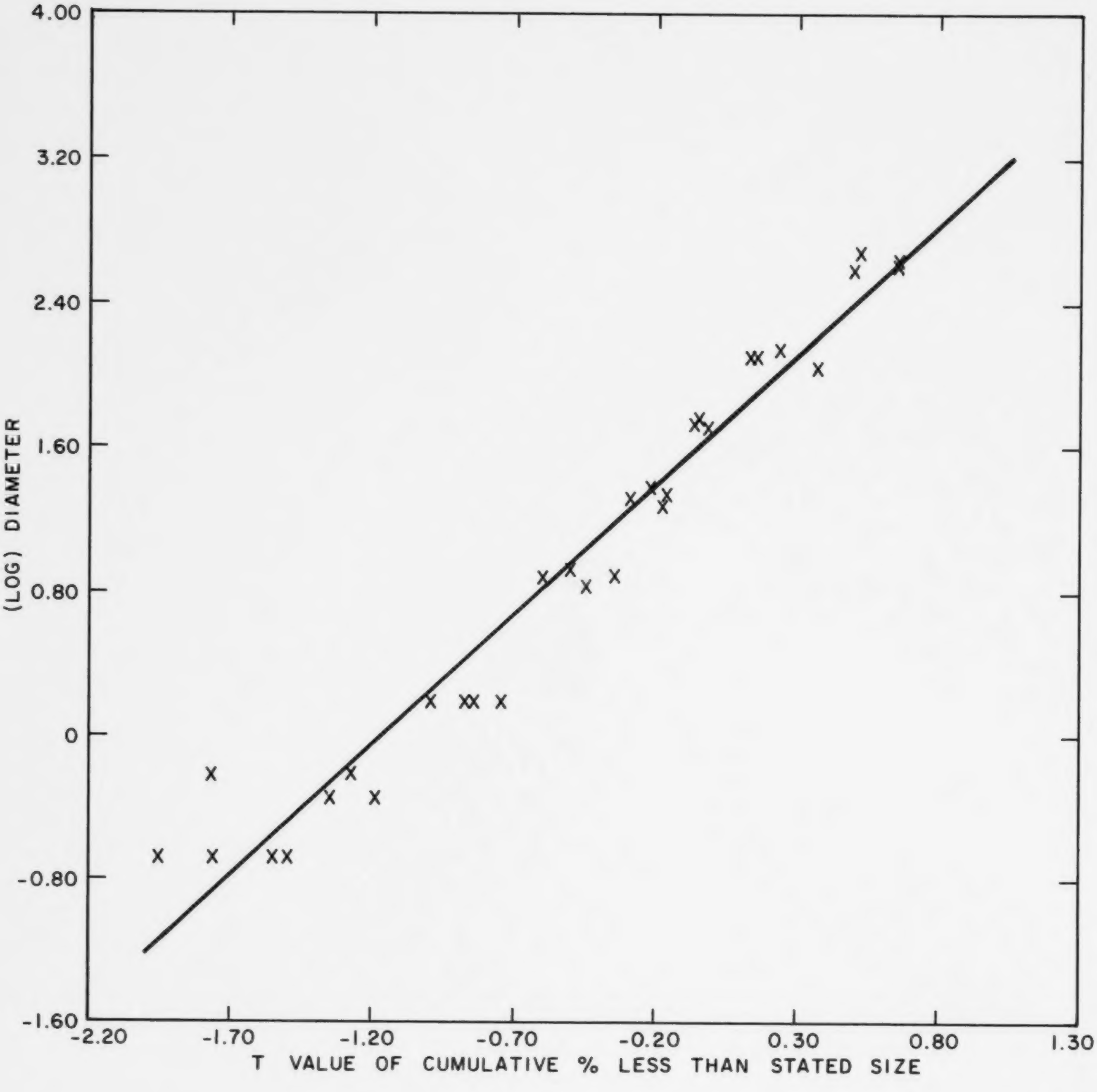


Figure 10. Particle size distribution (based on graph diameters) least squares fit vs. observed values - 4 selected runs

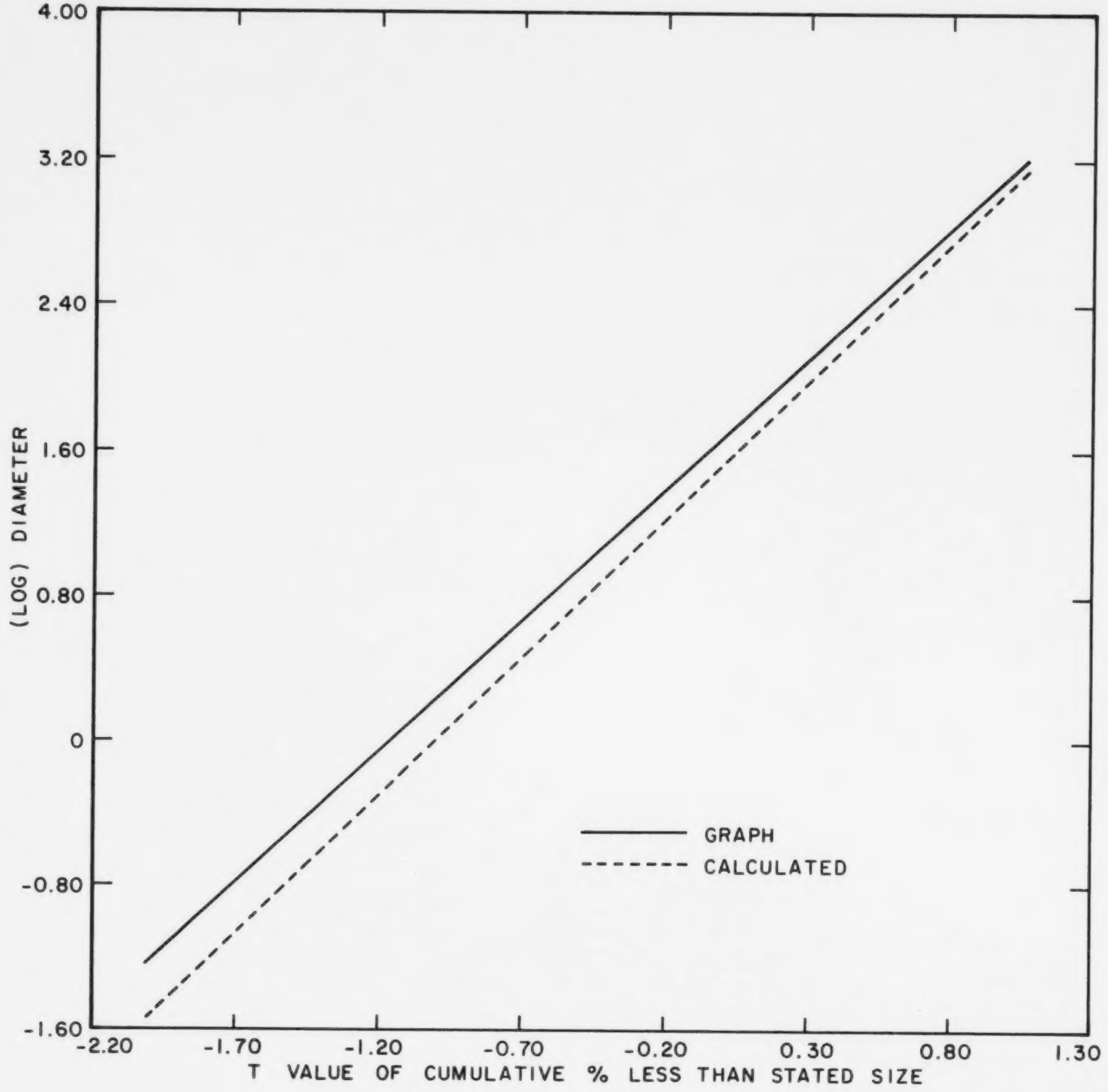


Figure 11. Comparison of fitted size distributions graph diameters vs. calculated diameters - 4 selected runs

TABLE 24. CHEMICAL ANALYSIS OF AAF ESP INLET FINE PARTICULATE
ANDERSEN IMPACTOR

Element	Particle >3 µm, µg/g 1	2	Particles 1-3 µm, µg/g 1	2	Particles <1 µm, µg/g 1	2
Al	85,600	38,900	76,300	30,400	50,700	29,200
Sb	1.90	1.64	<2.52	<1.85	3.84	<2.06
As	159	31.6	202	25.9	115	53.7
Ba	2,190	2,100	2,130	1,930	3,640	1,420
Be	5.79	1.73	5.12	1.73	3.11	1.73
B	683	868	198	2,250	2,070	679
Ca	16,000	19,200	15,900	28,200	26,100	16,800
Cd	2.44	2.37	3.51	0.963	5.75	3.17
Cl	18,000				32,000	
Cr	98.6	43.4	79.2	40	60.9	42.0
Co	175	46.9	75.6	536	56.2	41.3
Cu	112	53.5	131	38.4	135	30.4
F	49					
Fe	41,700	11,000	29,900	8,330	14,700	6,910
Pb	67.2	22.9	60.4	22.6	47.1	27
Mg	8,500	8,570	9,690	12,400	11,600	8,710
Mn	126	61.6	112	54.5	75.2	42.9
Hg	0.3	0.08	0.3	0.07	0.2	0.08
Ni	96.2	52.1	81.1	38.1	59.3	32.6
K	18,000	7,880	17,800	6,530	12,000	6,410
Se	17.5	5.86	11.6	2.96	2.43	<2.06
Na	51,300	77,100	92,800	117,700	97,000	95,000
Tc	194	1,310	3,500	727	1,950	952
V	168	51.6	156	31	104	49.6
Zn	611	841	694	809	1,280	557

MASS BALANCE

About 75 tons per hour of coal are fed into the Kingston Steam Plant Unit 6, and about 18 percent of this is ash. The ash content in pulverized coal was a key factor in estimating flows. The daily rates are given in Table 25.

TABLE 25. PERCENT ASH IN PULVERIZED COAL

Test	Ash%
114	18.9
115	17.1
117	16.5
119	19.0
120	18.8
121	17.0
122	17.8

When the mass flows were constrained to balance (as described below), the bottom ash to fly ash split was estimated to be 29.8. Table 26 gives the other splits involved.

TABLE 26. ASH DEPOSITION AND SPLIT IN WASTE STREAMS

Streams	Average Flow (lb/h)	Percent
Pulverized coal	27080	-
Bottom ash	8081	29.8
Mechanical collector	16060	59.3
ESP1 hopper	2584	9.5
ESP2 hopper	350	1.3
		99.9

The resulting 30/70 percent bottom ash/fly ash split is consistent with other studies of the Kingston plant.[3]

A more detailed summary is given in Table 27. There are some dependencies in the figures in that table. For example, except for rounding, the bottom ash and mechanical collector ash flows are constrained, i.e., sum of the ash flow in pulverized coal, less the ash flow at the inlet to the first ESP. The deposition in the first ESP is obtained by subtraction and in the second by assuming 99 percent collection efficiency.

ESTIMATION OF FLOWS

Flow rates were measured for whole and pulverized coal and for major points of ash flow. An initial material balance for total ash produced closures of only 50 percent. Whole coal and pulverized coal flow, although known to be subject to variability that require long sampling durations, were considered accurate. The particulate sampling at the inlet to the two ESPs was performed using EPA Method 5 and the results were also considered accurate. It was decided that errors occurred in the ash sluicing measurements, but no particular source of error has yet been ascribed.

To proceed with the analysis, flow rates for the sluiced ash streams were estimated. The hopper flow in the first ESP was obtained by subtracting outlet from inlet. The hopper flow in the second ESP was based on an assumed 99 percent collection efficiency for that precipitator.

The combined ash flow in the boiler and mechanical collector was made to equal the difference between ash flow in pulverized coal and flow into the first ESP.

The individual bottom ash and mechanical collector flows were calculated in three steps:

1. Estimation of bottom ash deposition rate (B) and mechanical collector efficiency (M), both expressed as a percentage.

2. Calculation of the proportion of ash in pulverized coal found in bottom ash and in the mechanical collector [these proportions are B and M (100-B), respectively].

3. Multiplication of these proportions by the ash flow rate from the pulverizer.

To estimate B and M in step 1, it is assumed that total ash is conserved. This leads to the equation:

$$B + M\,(100-B) = 100 - \frac{\text{(ash entering first ESP)}}{\text{(total ash in pulverized coal)}}.$$

Since two equations are needed to solve for the two variables B and M, an additional restriction was placed on B and M. This is the reasonable but arbitrary condition that the bottom ash deposition rate and mechanical collector efficiency have a constant ratio, reflecting nominal rates of 30 percent and 85 percent, respectively. That is:

$$B/M = 30/85.$$

Solving these equations for each day's ash and flow data resulted in bottom ash estimates of from 29.4 percent to 30.3 percent.

Thus, this approach is consistent with the simpler assumption of a 30 percent/70 percent bottom ash/fly ash split. The calculated split does not change appreciably from day to day. Similarly, the ash entering the first ESP is stable from day to day, being from 9.9 percent to 11.8 percent of the ash in pulverized coal.

TABLE 27. MASS FLOW RATES

Measured or Calculated	Flow	Minimum	Mean	Maximum	Standard Deviation	Relative Standard Deviation
M	Whole coal (t/h)	71.6	76.10	79.4	2.74	3.6
C	Pulverized coal (t/h)	71.2	75.66	78.9	2.72	3.6
M	Pyrites (lb/h)	708	867.1	981	90.7	10.5
C	Ash in pulverized coal (lb/h)	23500	27080	30000	2440	9.0
C	Bottom ash (lb/h)	7060	8081	8880	717	8.9
C	Mechanical collector (lb/h)	14000	16060	17700	1430	8.9
M	Inlet to first ESP (lb/h)	2450	2938	3390	363	12.4
C	First ESP hopper (lb/h)	2200	2584	2880	229	8.9
M	Outlet of first ESP (Lb/h)	111	354	581	160	45.2
C	Second ESP hopper (lb/h)	110	350	576	158	45.2
M	Outlet of second ESP (lb/h)	1	20	46	17.6	87.2

To determine flows for individual elements, the ash flow rates--bottom ash, mechanical collector and ESP hoppers--were multiplied by the measured elemental concentrations in each stream to obtain a pound-per-hour flow of each element in each stream. The flow rates for each element are shown in Table 28 and Table 29. As a result, within each waste stream, the relative abundances of elements depend only on chemical concentration measurements, not on assumptions about flows or flow calculations. However, estimates of relative deposition of an element in the various streams do depend on these assumptions.

SULFUR BALANCE

It was a recommendation[4] of a TVA study at the Colbert Steam Plant to measure sulfur in the gaseous phase and to perform a sulfur balance. The daily results (Table 30) show balances between 83 percent and 105 percent, with an outlying value of 173 percent on test day 119. All tabled entries are based on measurements, except the balance figures, which include calculated sulfur flows in the four ash waste streams (not tabled).

TABLE 30. MEASURED SULFUR FLOWS AND MASS BALANCE

Test Number*	Sulfur in Whole Coal (lb/h)	Gaseous Sulfur (lb/h)	% S in Flue Gas	Balance (%)
114	3740	2900	78	88
115	3340	2870	86	93
119	3050	4840	159	173
120	2860	2490	87	98
121	3360	3200	95	106
122	3560	2570	72	83

*Sulfur was not measured in whole coal on test number 117.

There is no good explanation for the large SO_2 recording on test day 119.

FLOWS AND BALANCES FOR INDIVIDUAL ELEMENTS

Elements of Concern

Table 31 lists elements of environmental concern and the average flow rate for each element in the whole coal.

Aggregation of Elements

As an omnibus test of conservation of elements given the method of estimating flow for total ash, the flows for all of the measured elements (except sulfur) were added and compared in the pyrites and ash streams.

TABLE 28. FLOWS OF TRACE ELEMENTS FOR WHOLE COAL, PULVERIZED COAL, PYRITES AND BOTTOM ASH (POUNDS PER HOUR)

Test	Ag	Al	As	B	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe
							WHOLE COAL							
114	0.77	3760	2.92	11.7	26.7	0.25	348.4	0.0215	102.8	2.30	4.60	4.91	21.33	2455
115	1.47	3600	1.91	9.3	28.5	0.25	273.3	0.0206	88.2	2.20	4.26	4.41	21.30	2130
117														
119	0.79	4365	3.17	12.7	35.6	0.27	290.5	0.0190	104.8	2.38	4.76	4.76	24.45	2714
120	0.78	4213	1.86	10.3	33.7	0.27	235.6	0.0110	90.5	2.34	4.52	4.21	24.50	1919
121	0.76	3257	1.06	10.2	25.0	0.21	312.1	0.0212	90.0	3.03	3.79	3.64	22.12	2060
122	0.78	4200	2.02	12.3	30.3	0.25	284.7		146.2	3.89	5.29	5.45	24.42	2426
							PULVERIZED COAL							
114	0.76	3815	1.98	11.60	30.37	0.26	280.8	0.03	91.57	2.29	4.27	4.27	21.67	2150
115	2.92	3285	1.75	10.36	30.36	0.23	259.8	0.02	119.70	1.46	3.65	3.80	21.61	2057
117	0.71	3203	1.57	10.25	26.19	0.23	269.0	0.02	119.60	2.85	3.42	3.70	20.21	1849
119	0.79	3944	2.52	12.31	29.66	0.27	293.4	0.02	108.90	3.16	4.26	4.10	23.35	2491
120	0.78	4038	1.71	10.25	26.56	0.30	284.2	0.02	96.30	2.33	4.50	4.19	23.45	1769
121	0.75	3466	1.66	10.25	25.92	0.24	304.4	0.03	75.30	1.51	3.77	3.47	19.74	1987
122	0.77	3713	1.55	11.40	31.70	0.23	321.8	0.02	92.80	1.55	4.18	3.87	22.43	2336
							PYRITES							
114	0.01	12	0.11	0.39	0.09	0.00	10.9	0.0004	0.13	0.02	0.03	0.02	0.06	89
115	0.01	14	0.12	0.43	0.10	0.00	12.0	0.0004	0.14	0.02	0.03	0.03	0.06	98
117	0.01	13	0.12	0.41	0.09	0.00	11.3	0.0004	0.13	0.02	0.03	0.03	0.06	93
119	0.01	12	0.17	0.45	0.08	0.00	9.8	0.0002	0.10	0.04	0.04	0.03	0.06	98
120	0.01	9	0.12	0.33	0.06	0.00	7.1	0.0001	0.07	0.03	0.03	0.02	0.04	71
121	0.01	10	0.14	0.37	0.07	0.00	8.0	0.0002	0.08	0.03	0.03	0.02	0.05	80
122	0.01	11	0.15	0.42	0.07	0.00	9.1	0.0002	0.09	0.04	0.04	0.03	0.05	91
							BOTTOM ASH							
114	0.04	1136	0.06	2.03	7.58	0.07	73.1	0.0005	0.06	0.61	1.35	0.92	0.09	813
115	0.07	991	0.05	1.70	7.78	0.06	62.2	0.0030	0.06	0.51	1.06	0.80	0.07	704
117	0.11	952	0.03	1.80	7.40	0.06	67.2	0.0020	0.06	0.53	1.02	0.75	0.07	712
119	0.09	1154	0.04	2.22	8.22	0.07	75.1	0.0019	0.05	0.71	1.29	0.98	0.09	858
120	0.04	1119	0.06	1.76	7.09	0.07	60.5	0.0019	0.22	0.65	1.32	0.96	0.09	664
121	0.04	1008	0.03	1.88	6.94	0.06	74.9	0.0011	0.04	0.58	1.20	0.84	0.08	756
122	0.04	1066	0.04	2.06	8.28	0.06	77.6	0.0018	0.04	0.57	1.20	0.90	0.08	845

TABLE 28. (Continued)

Hg	K	Mg	Mn	Na	Ni	Pb	S	Sb	Se	Si	Ti	V	Zn
WHOLE COAL													
0.099	733.5	198.0	10.89	58.3	3.68	2.32	3740	0.17	0.74	7380	216.4	7.52	3.84
0.060	775.7	199.8	5.89	55.8	3.53	2.03	3340	0.26	0.66	7050	202.8	7.35	3.67
0.043	782.6	219.1	6.52	76.2	3.17	2.60	3050	0.22	0.78	8780	238.1	7.94	5.08
0.041	823.8	213.8	6.85	68.6	3.12	3.01	2860	0.16	0.75	8750	227.8	7.33	4.37
0.033	595.3	175.7	5.17	60.6	2.73	2.53	3360	0.24	0.73	6510	183.3	6.21	4.54
0.047	833.8	241.1	9.63	71.6	5.60	2.68	3562	0.22	0.70	8462	231.8	7.47	3.89
PULVERIZED COAL													
0.087	824.1	204.5	5.54	64.1	2.75	2.81	3387	0.12	1.05	8149	241.1	7.63	4.12
0.032	677.4	181.0	4.93	52.5	2.63	2.09	2978	0.26	0.78	6700	200.0	6.72	3.36
0.037	580.7	173.7	4.21	54.1	2.56	2.28	2775	0.21	0.80	6049	183.6	6.41	3.27
0.035	864.5	209.8	5.74	72.6	3.16	2.59	3044	0.54	1.09	8235	233.5	7.57	4.26
0.028	815.4	201.9	5.03	62.1	2.80	2.42	2562	0.17	1.09	8417	242.3	7.61	3.88
0.027	783.5	171.8	5.80	57.3	2.56	2.62	2817	0.15	1.13	6870	198.9	6.48	3.77
0.034	741.0	201.1	6.31	58.8	2.63	2.17	3125	0.15	1.05	7085	215.0	7.58	3.25
PYRITES													
0.0006	2.5	1.5	0.22	0.2	0.02	0.09	346	0.00	0.01	47	1.1	0.05	0.05
0.0007	2.8	1.7	0.25	0.3	0.03	0.10	381	0.00	0.01	52	1.2	0.05	0.06
0.0007	2.7	1.6	0.23	0.3	0.02	0.10	360	0.00	0.01	49	1.1	0.05	0.06
0.0009	2.4	1.2	0.29	0.3	0.03	0.10	399	0.00	0.02	42	1.0	0.06	0.06
0.0006	1.7	0.9	0.21	0.2	0.02	0.07	288	0.00	0.01	30	0.7	0.04	0.04
0.0007	2.0	1.0	0.23	0.2	0.02	0.08	327	0.00	0.01	34	0.8	0.05	0.05
0.0008	2.2	1.1	0.26	0.2	0.02	0.09	369	0.00	0.01	39	0.9	0.05	0.05
BOTTOM ASH													
0.0009	179.1	53.7	1.95	15.7	0.99	0.54	16	0.01	0.02	2342	64.8	1.96	1.05
0.0007	141.7	49.0	1.76	13.2	0.81	0.34	8	0.01	0.01	1960	53.3	1.70	0.32
0.0007	144.5	50.0	1.61	13.4	0.86	0.26	5	0.01	0.01	1924	51.7	1.61	0.46
0.0009	190.8	58.8	2.01	16.0	0.92	0.45	10	0.01	0.04	2467	64.4	2.04	0.38
0.0009	182.5	55.4	1.87	14.6	0.91	0.31	7	0.01	0.02	2488	66.4	1.96	0.37
0.0008	169.1	50.4	2.38	14.0	0.88	0.35	8	0.01	0.01	2172	58.0	1.75	0.29
0.0008	160.7	56.5	2.12	14.8	0.92	0.46	8	0.01	0.01	2190	58.8	1.89	0.38

TABLE 29. FLOWS OF TRACE ELEMENTS FOR MECHANICAL COLLECTORS, RC ESP HOPPER AND AAF ESP HOPPER (POUNDS PER HOUR)

Test	Ag	Al	As	B	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe
MECHANICAL COLLECTOR														
114	0.17	2156	0.83	4.21	16.02	0.16	161.4	0.0036	0.24	0.17	2.57	2.28	0.17	1376
115	0.15	1762	0.63	3.45	16.88	0.14	145.8	0.0031	0.28	0.37	2.14	2.06	0.15	1308
117	0.14	2030	0.95	3.36	14.28	0.13	147.0	0.0035	0.53	1.05	2.03	2.00	0.14	1218
119	0.18	2479	1.20	4.27	16.15	0.15	161.9	0.0041	0.57	1.42	2.55	2.18	0.18	1488
120	0.17	2583	0.83	3.25	14.00	0.15	118.5	0.0029	0.50	1.21	2.55	2.13	0.17	1076
121	0.38	2141	1.02	3.47	13.43	0.13	157.5	0.0050	0.32	1.07	2.19	1.96	0.35	1228
122	0.16	2280	0.85	3.86	16.09	0.13	171.0	0.0049	0.28	1.38	2.31	2.10	0.16	1402
RC ESP HOPPER														
114	0.04	346	0.32	0.56	2.52	0.03	23.8	0.0042	0.02	0.14	0.40	0.49	0.17	159
115	0.03	372	0.32	0.75	2.66	0.03	25.9	0.0037	0.01	0.16	0.41	0.45	0.11	192
117	0.03	309	0.21	0.57	2.36	0.02	23.8	0.0046	0.02	0.12	0.38	0.46	0.25	149
119	0.03	404	0.40	0.87	2.74	0.03	26.0	0.0046	0.13	0.14	0.45	0.53	0.25	183
120	0.03	402	0.28	0.77	2.38	0.03	21.8	0.0039	0.02	0.18	0.42	0.50	0.24	155
121	0.02	342	0.34	0.67	2.29	0.03	21.8	0.0049	0.02	0.12	0.38	0.44	0.28	142
122	0.03	373	0.37	0.69	2.72	0.03	27.2	0.0061	0.01	0.15	0.41	0.49	0.42	162
AAF ESP HOPPER														
114	0.00	54	0.06	0.12	0.32	0.00	3.0	0.0012	0.00	0.02	0.06	0.07	0.07	22
115	0.02	41	0.06	0.09	0.29	0.00	2.8	0.0012	0.00	0.02	0.05	0.06	0.08	17
117	0.01	35	0.05	0.08	0.26	0.00	2.8	0.0009	0.00	0.02	0.04	0.05	0.05	15
119	0.01	71	0.09	0.18	0.51	0.01	4.9	0.0023	0.01	0.03	0.09	0.10	0.10	30
120	0.01	83	0.10	0.19	0.56	0.01	5.3	0.0021	0.01	0.04	0.10	0.11	0.21	32
121	0.00	16	0.02	0.04	0.11	0.00	1.1	0.0006	0.00	0.01	0.02	0.02	0.06	6
122	0.01	53	0.07	0.12	0.41	0.00	4.0	0.0015	0.00	0.02	0.07	0.08	0.06	22

TABLE 29 (Continued)

Hg	K	Mg	Mn	Na	Ni	Pb	S	Sb	Se	Si	Ti	V	Zn
MECHANICAL COLLECTOR													
0.0017	419.1	116.8	3.07	34.5	1.91	1.26	15	0.03	0.03	5140	134.2	4.62	1.62
0.0032	358.3	104.4	2.95	29.4	1.69	1.21	12	0.05	0.02	4258	110.7	3.98	1.34
0.0017	284.1	100.4	2.53	29.4	1.72	1.03	12	0.03	0.05	3905	101.3	3.88	1.41
0.0018	391.4	121.5	3.38	33.6	1.91	1.20	16	0.04	0.04	5153	128.6	4.83	1.77
0.0017	371.9	116.6	2.96	31.0	1.83	1.30	15	0.05	0.05	5165	130.2	4.36	1.72
0.0015	296.7	103.7	3.46	30.6	1.61	1.06	12	0.05	0.05	4328	111.3	3.90	2.00
0.0024	301.3	112.4	3.26	34.2	1.73	1.24	19	0.04	0.05	4283	114.3	3.92	1.50
RC ESP HOPPER													
0.0004	53.7	18.6	0.51	5.7	0.33	0.25	6	0.01	0.01	569	18.3	0.77	0.52
0.0005	46.0	20.2	0.56	6.4	0.37	0.32	7	0.01	0.01	603	20.1	0.79	0.65
0.0003	48.1	17.4	0.60	5.3	0.30	0.25	5	0.01	0.02	506	16.6	0.73	0.54
0.0006	58.3	22.8	0.59	7.2	0.35	0.39	8	0.01	0.02	681	21.2	0.85	0.80
0.0006	62.4	21.4	0.53	6.1	0.36	0.31	6	0.01	0.03	688	20.5	0.81	0.66
0.0006	59.5	19.2	0.59	6.3	0.31	0.29	7	0.01	0.02	620	18.7	0.71	0.51
0.0006	62.7	21.1	0.64	6.9	0.34	0.29	7	0.01	0.03	648	20.1	0.79	0.55
AAF ESP HOPPER													
0.0001	8.7	2.7	0.07	0.9	0.05	0.05	1	0.00	0.01	93	2.8	0.12	0.10
0.0000	5.7	2.1	0.06	0.7	0.05	0.04	1	0.00	0.00	64	2.1	0.10	0.09
0.0000	5.1	1.9	0.06	0.7	0.04	0.03	1	0.00	0.00	54	1.8	0.08	0.07
0.0001	9.7	4.1	0.11	1.4	0.07		2	0.00	0.01	117	3.7	0.16	0.20
0.0001	11.3	4.7	0.13	1.4	0.09	0.08	3	0.00	0.01	132	4.4	0.19	0.19
0.0000	2.2	0.9	0.03	0.3	0.02	0.02	1	0.00	0.00	26	0.9	0.04	0.04
0.0001	9.9	3.1	0.09	1.0	0.06	0.05	2	0.00	0.01	81	2.9	0.12	0.18

TABLE 31. SELECTED TRACE ELEMENT FLOW RATES

Element	Flow (lb/h)	Element	Flow (lb/h)
V	7.30	Ag	0.89
Cu	4.56	Se	0.73
Cr	4.54	Be	0.25
Zn	4.23	Sb	0.21
Ni	3.64	Hg	0.05
Pb	2.53	Cd	0.02
As	2.16		

Based on the average of the flows over six test days, balances from 87.5 to 106.3 percent were found with an average of 96.7 percent. The daily balances are shown in Table 32.

TABLE 32. DAILY MASS BALANCE

Test Day	Balance (%)
114	103.1
115	94.8
119	94.6
120	96.6
121	106.3
122	87.5

Balances of Individual Elements

Table 33 gives the mass balances on a whole unit basis for the measured elements (averaged over test days). The list is arranged by decreasing order of balance. The abundances of these elements in whole coal are given in the rank column.

Relative Abundance of Elements

The rankings in the Table 33 illustrate the relative abundance of elements in whole coal. For pyrites and the four ash streams, the seven most abundant elements are shown in Table 34 with the concentration expressed as a percentage. It should be noted these rankings and percentages depend only on the measured concentrations, not on estimated flows.

TABLE 33. BALANCE OF INDIVIDUAL ELEMENTS

Rank	Element	Balance (%)	Rank	Element	Balance (%)
4	Fe	103.7	21	Pb	82.6
1	Si	99.8	16	Cu	79.8
15	V	97.6	5	K	79.2
2	Al	96.5	22	As	77.3
25	Be	96.3	18	Zn	69.6
7	Ti	95.4	20	Co	65.8
3	S	94.2	28	Cd	65.1
8	Mg	92.5	13	B	62.8
17	Cr	91.7	23	Ag	36.1
6	Ca	90.2	26	Sb	31.8
19	Ni	89.7	24	Se	13.9
11	Ba	88.1	27	Hg	8.8
14	Mn	87.5	12	F	2.9
10	Na	84.4	9	Cl	0.6

TABLE 34. RELATIVE ABUNDANCE OF ELEMENTS

Pyrites		Bottom Ash		Mechanical Collector		First ESP Hopper		Second ESP Hopper	
Elem.	%	Elem.	%	Elem.	%	Elem.	%	Elem.	%
S	69.3	Si	50.0	Si	51.6	Si	48.0	Si	47.1
Fe	17.3	Al	23.9	Al	24.7	Al	28.4	Al	29.3
Si	8.0	Fe	17.2	Fe	14.6	Fe	12.7	Fe	11.9
Al	2.2	K	3.8	K	3.9	K	4.3	K	4.4
Ca	1.9	Ca	1.6	Ca	1.7	Ca	1.9	Ca	2.0
K	0.5	Ti	1.3	Ti	1.3	Mg	1.6	Mg	1.6
Mg	0.2	Mg	1.2	Mg	1.2	Ti	1.5	Ti	1.5

Preferential Deposition

It is of interest whether some elements tend to concentrate in specific waste streams. Some preferential deposition is obvious; for example, sulfur in solid form is found more in pyrites than in any of the waste streams. However, except for sulfur and other elements that volatilize, the relative deposition of an element in the various waste streams tends to follow the total flows in these streams. These ideas were quantified and explored as follows. First, the total flow in each stream was computed as the sum of the average pound per hour flows for the 28 elements measured. Next, the relative deposition in each waste stream was computed as the total flow in the waste stream expressed as a percentage of the total flow in whole coal. For example, over the test days, the average total flows for whole coal and bottom ash were 19070 lb/h and 4520 lb/h, respectively. Thus, the relative deposition in the bottom ash is 23.7 percent. The relative depositions are shown in the first column of Table 35. The relative deposition for a single element was computed similarly. For example, the average flow of iron was 2284 lb/h and 773.1 lb/h in whole coal and the bottom ash, respectively, giving a relative deposition of 33.8 percent. For the mechanical collector, ESP hoppers and pyrites, the respective percentages are 57.5, 7.24, 0.93, and 3.85.

The relative depositions for many of the elements, not just abundant elements like iron, follow the same pattern as for total flow--the largest deposition occurs in the mechanical collector, followed by bottom ash, the first ESP hopper, pyrites and the second ESP hopper. To measure a preference for an element to deposit in a waste stream, that element's relative deposition is compared to the relative deposition in the waste stream. The resulting numerical difference can be thought of the relative excess or deficiency of an element in a waste stream. For iron, in pyrites, bottom ash, the mechanical collector and the ESP hoppers, these differences are, respectively, 1.19, 10.1, 9.8, 0.34, and 0.02 percent. These are plotted in the panel for iron in Figure 12, which summarizes the relative deposition for all the elements studied.

TABLE 35. RELATIVE DEPOSITION OF As, Cd, Pb, and Zn

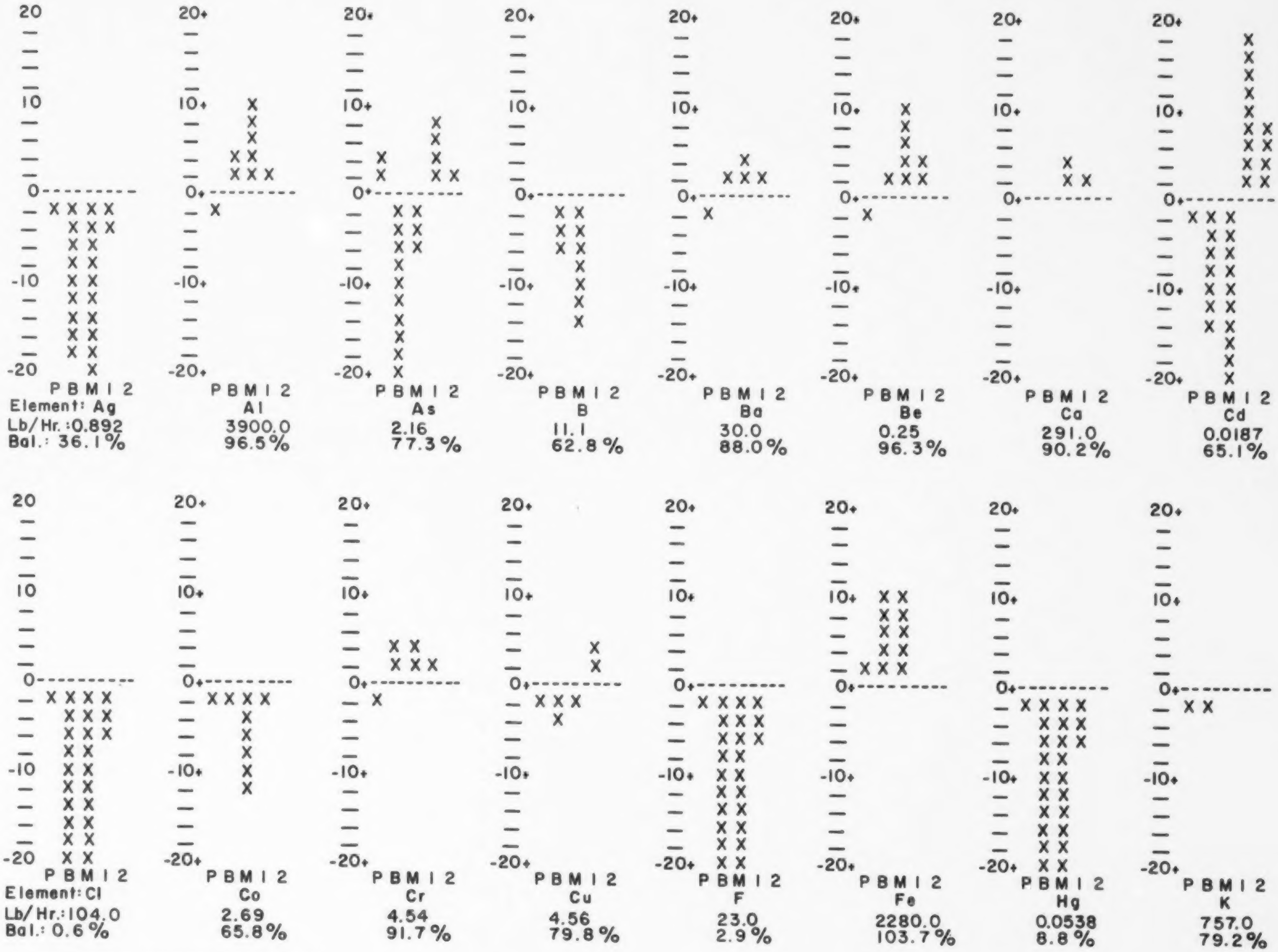
	Percentage of the Incoming Material				
Waste Stream	Ash	As	Cd	Pb	Zn
Pyrites	2.66	6.3	1.3	3.6	1.2
Bottom ash	23.7	2.1	9.1	16.1	11.0
Mechanical collector	47.7	41.4	21.1	47.9	38.4
First ESP hopper	6.9	15.7	24.5	12.2	14.3
Second ESP hopper	0.95	3.1	8.0	1.8	2.9

The more interesting panels are those where deposition in some ash streams is below the trend and above in other streams. This occurs for arsenic, cadmium, and lead. A summary for these and other elements of environmental interest is as follows.

Arsenic, Cadmium, Lead, and Zinc: There is a shortfall in bottom ash and the mechanical collector and, for arsenic and cadmium, an abundance in the ESP hoppers. The split for these elements and the total metal constituents are shown in Table 35.

Mercury, Antimony, and Selenium: A shortfall attributed to volatilization, occurs in all ash streams.

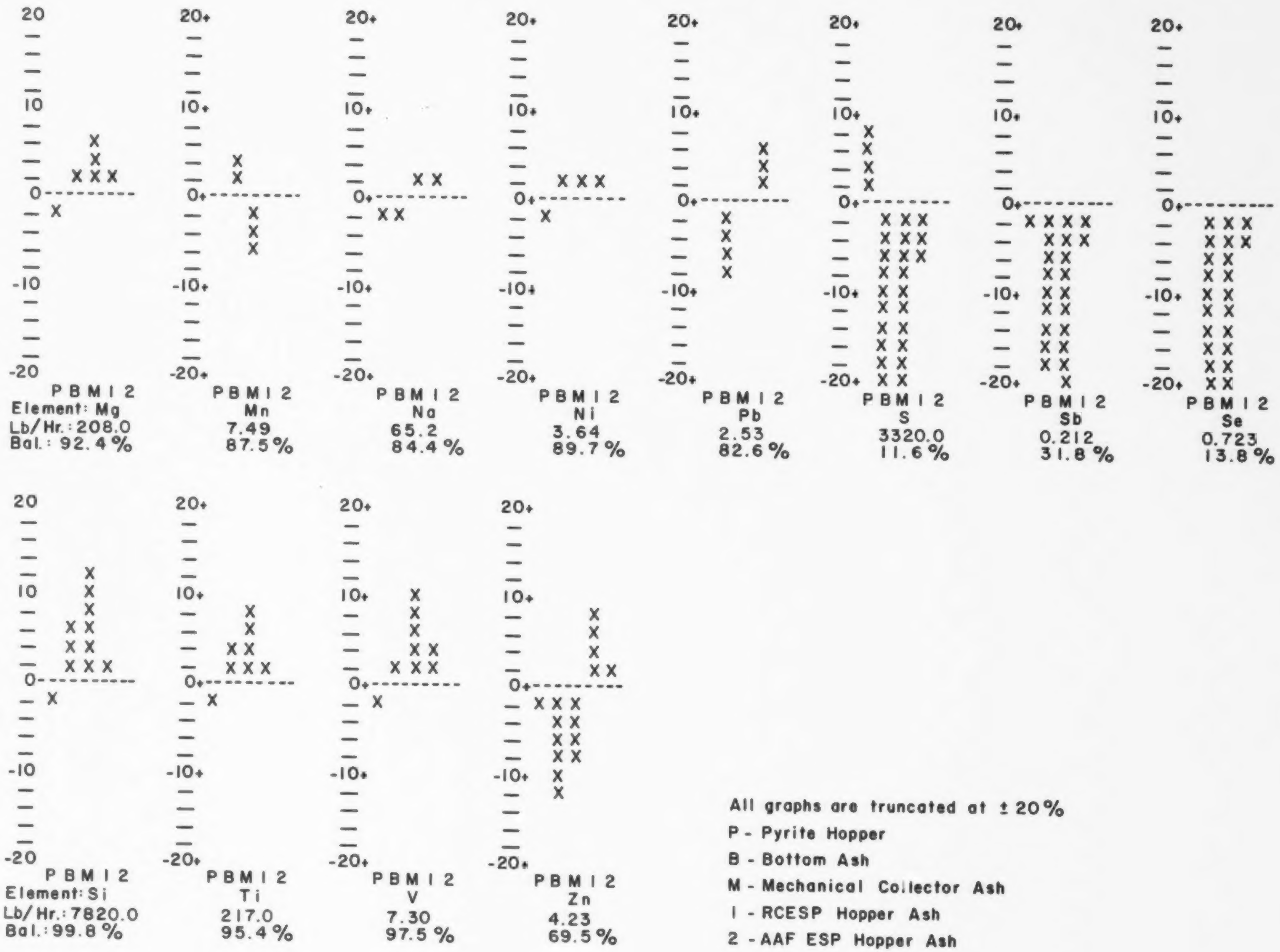
There were no remarkable deviations from the relative deposition for the remaining elements. Although another study[6] reports many elements which showed preferential deposition the results from this work indicates only cadmium was shown to be enriched in the ash collected by either ESP.



All graphs are truncated at ± 20%

P - Pyrite Hopper, B - Bottom Ash, M - Mechanical Collector Ash, 1 - RCESP Hopper Ash, 2 - AAF ESP Hopper Ash

Figure 12. Difference in proportional deposition between each element and total flow



All graphs are truncated at ± 20%

P - Pyrite Hopper

B - Bottom Ash

M - Mechanical Collector Ash

I - RCESP Hopper Ash

2 - AAF ESP Hopper Ash

Figure 12 (continued)

CLUSTER ANALYSIS

For each test day or average over test days, the elemental concentration data can be cross-classified by waste stream and element. Clustering of each of these classifying variables answers the questions of which streams behave similarly and which elements behave similarly. There is a wealth of clustering procedures, many based on heuristic principles of "distance" or ranking in a multidimensional space of variables. To cluster waste streams, the relationships among elements are explored; to cluster elements, the roles are reversed. Clustering[5] is a descriptive tool that need not be based on probability models. Accordingly, the notion of "statistical significance" is most often inappropriate. It is not used below.

Clustering Waste and Other Streams

The purpose of this analysis was to confirm expected similarity in and differences between coal and ash streams. A hierarchical approach was taken, which in a stepwise fashion assigns streams to a smaller number of clusters until all are categorized into one cluster. By observing which streams are clustered together as the procedure progresses, an indication of relative similarity is afforded. The variables used to cluster the streams were the logarithms of the average elemental concentrations.

As Figure 13 shows, the first cluster of more than one stream includes whole and pulverized coal. The second contains the two ESP hoppers, and the third contains bottom ash and the mechanical collector. The pyrites do not join a cluster until near the end of the process. These results are not surprising; the failure to obtain them would have provided an occasion to examine the data for discrepancies.

Clustering of Elements

In the clustering of the elements, two techniques were used. The first method ranked each stream according to the concentration of a given element. Each element is associated with a sequence of ranks, and elements can be grouped according to rankings and group of rankings they share. The second method is based on the lb/h flows of each element for each element and the relative patterns noted in the deposition.

Using the first method, Table 36 below shows silicon to be 27.5 percent of the bottom ash (BA), 28.6 percent of the mechanical collector ash (MC), 23.8 percent of the ash in the first ESP hopper (H1), and 23.1 percent of the ash in the second ESP hopper (H2). Thus, in silicon concentration the mechanical collector ranks largest, followed by bottom ash and the two ESP hoppers, in order. Ranks were assigned to these four streams--a rank of 1 for the smallest concentration and a rank of 4 for the largest--resulting in the ranks 3, 4, 2, and 1, seen in the column under silicon in Table 37.

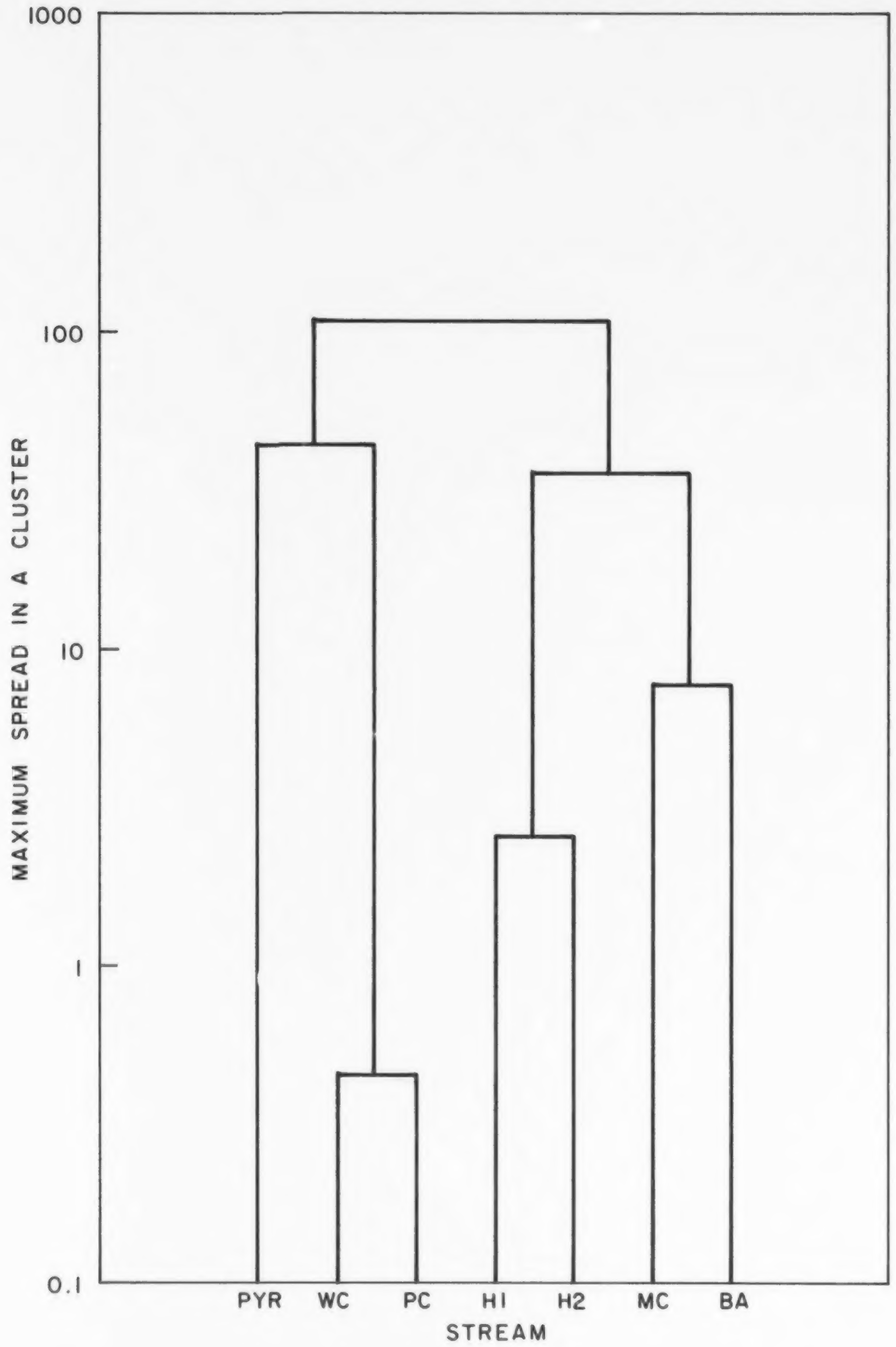


Figure 13. Waste stream cluster analysis

TABLE 36. AVERAGE CONCENTRATION OF ALUMINUM, IRON, AND SILICON

Stream	Al	Fe	Si
Percent of Measured Elements			
BA	13.1	9.5	27.5
MC	13.7	8.1	28.6
H1	14.1	6.3	23.8
H2	14.4	5.8	23.1

TABLE 37. RANKS BASED ON COLUMNS FROM TABLE 36

Stream	Al	Fe	Si
BA	1	4	3
MC	2	3	4
H1	3	2	2
H2	4	1	1

This ranking process was done for all the elements measured except silver, fluorine, and mercury, which exhibited a number of concentrations below detection limits. The resulting rank patterns provide a basis for clustering. For example, the rank patterns for aluminum, iron, and silicon, taken from the columns of Table 37, are 1234, 4321, and 3421, respectively. The clustering of all elements is as follows:

Rank Pattern	Element(s)*	
3421	Si	Lower concentrations in the ESP hoppers
4321	Fe	
1234	Al As Ba Be Cd Cu Mg Na Pb Sb Se Ti V Zn	Higher concentrations in the ESP hoppers
2134	B Cr Ni S	
1234	K	
1324	Ca	Mixed behavior
1432	Cl	
4213	Co	
4123	Mn	

---

*Silver, fluorine, and mercury were excluded because they exhibited a number of concentrations below detection limits.

The second method of clustering, in view of the various patterns in Figure 12, reveals four archetypical patterns. These patterns exclude the pyrites hopper because this deposition occurs prior to the combustion of the coal and the trends established from the high temperature encountered during combustion would not necessarily relate to the trends established in the pulverizers. An example of this situation would be encountered with sulfur because it is preferentially deposited in the pyrite hopper whereas after combustion major losses are reported in all streams. The groups of elements will be described in the descending order of size.

The first archetypical pattern shows larger gains in the ash sampled at the mechanical collector with lesser gains in the bottom ash and the first ESP. The elements found in this group are Al, Ba, Be, Ca, Cr, Fe, Mg, Si, Ti, and V. This group contains the majority of the elements that form refractory oxides and most of the alkaline metals. The second archetypical pattern shows losses in all streams considered. This group contains Ag, Cl, F, Hg, S, Sb, and Se. This group represents the more volatile elements. The remaining two groups are much smaller in size. The next archetypical pattern shows a loss in both the bottom ash and the mechanical collector ash but shows a gain in both ESP's hopper ash. This group includes As, Cd, and Zn. The last archetypical pattern is very flat and shows little deviation from the total deposition of ash. This group consists of K, Na, and Ni. The remaining five elements (B, Co, Cu, Mn, and Pb) did not fit in any of the above groups and show no discernable trends.

DATA REDUCTION AND TREATMENT OF CONCENTRATIONS BELOW DETECTION LIMITS

As is common in analytical work, a number of concentrations fell below the detection level of laboratory analysis. Additionally, some values were not available for certain combinations of sampling points and concentration, either because no samples were scheduled or for unscheduled reasons. The samples can be cross-classified by test day and sampling points. The different identifiers for these are test days 114 through 122 and the following points: whole coal (WC), pyrites (PYR), pulverized coal (PC), bottom ash (BA), mechanical collector (MC), inlet to the first ESP (ESPI), first ESP hopper (ESPH1), outlet from the first ESP (ESPO1), second ESP hopper (ESPH2), outlet from the second ESP (ESPO2), and three vapor phase points (VAP1, VAP2, and VAP3). The following chart shows test-point combinations (marked by an X) where either samples or adequate data were not available. A discussion follows of the problems incurred and the data reduction actions that resulted.

1. No vapor phase data were obtained except on test 120 (VAP1), and tests 114 and 115 (VAP2 and VAP3). A number of "less than" values also occurred for concentrations in the vapor phase and in the second ESP outlet. Action: The vapor phase and ESPO2 data would not be used in the analysis (except for sulfur balances).

Test	Sample Point												
	WC	PYR	PC	BA	MC	ESPI	ESPH1	ESPO1	ESPH2	ESPO2	VAP1	VAP2	VAP3
114											X		
115										X	X		
116	X	X	X	X	X		X		X	X	X	X	X
117	X										X		
118		X	X	X	X	X	X	X	X	X	X	X	X
119										X	X	X	X
120										X		X	
121										X	X	X	X
122										X	X	X	X

2. On tests 116 and 118, no samples were taken of pyrites or ash streams. Action: These test days were dropped from the analysis.

3. No elemental analyses were done for whole coal on test 117. Action: Mass balance calculations on a whole unit basis. Ignore test 117.

4. Thallium was below detection limits (25 ppm) in all measurements. Silver was often below detection limits (5 ppm) in whole and pulverized coal. Fluorine and mercury were often below detection limits (20 and 0.1 ppm, respectively) in bottom ash and the mechanical collector. Action: Thallium was dropped from the analysis. For estimating total flows and mass balances, the silver, fluorine, and mercury concentrations were below detection limits and thus the detection limit concentration was used. For cluster, correlation and precision analyses, these three elements were dropped.

5. Two missing values were taken into consideration during statistical analysis (cadmium in whole coal on test 122, and lead in the second ESP hopper on test 119).

Precision of Measurement and Sampling

The data made available for analysis are subject to at least two kinds of variability. One is the natural variability in the environment exhibited, for example, in aluminum concentrations in bottom ash that vary somewhat from day to day. A second is the error (variation) introduced by laboratory analysis of a sample.

If there are no systematic errors in sampling or in laboratory determinations, then the combined environmental and analytical variations do not bias estimates of mean concentration. But if the relationship between variables in the environment is of interest, then analytical error will tend to mask it. For example, regression coefficients will be biased toward zero. This biasing effect is known as attenuation.

Since regression methods were not used in this study, the problem of attenuation does not apply to the results in this report. For readers of the report, the environmental variability of elemental concentrations and laboratory variability are still of interest for two reasons: First, for estimating means--estimates of variability are essential in determining the number of days of sampling to schedule and the number of duplicate determinations to carry out in the laboratory; secondly, in multivariate correlation analysis, the phenomenon of attenuation can be quantified and its effects partially adjusted.

Therefore, as a reference for use in future studies, laboratory coefficients of variation (CV's) and CV's for the data over time (given an element and waste stream) are listed in Tables 38 and 39. The latter set of CV's reflect both the day-to-day variability in a steam plant environment and measurement in the laboratory. The CV's in Table 38 were reported by the TVA Laboratory Branch. The CV's in Table 39 were calculated from the data analyzed in this report.

TABLE 38. LABORATORY COEFFICIENTS OF VARIATION (CV's)

Element	CV in Coal Measurements	CV in Ash Measurements
Al	4.0	4.2
As	1.1	4.6
B	3.0	4.8
Ba	2.8	3.1
Be	3.2	3.0
Ca	1.5	3.3
Cd	4.6	15.7
Cl	-	0.8
Co	51.8	37.5
Cr	3.4	3.4
Cu	12.2	3.8
Fe	1.7	1.9
K	8.9	8.4
Mg	2.4	1.7
Mn	7.1	2.5
Na	10.6	3.4
Ni	12.2	6.3
Pb	14.7	13.1
S	3.3	1.8
Sb	10.2	4.2
Se	5.8	7.6
Si	2.8	2.8
Ti	2.3	2.4
V	0.8	3.6
Zn	0.8	8.9

TABLE 39. COEFFICIENTS OF VARIATION OF CONCENTRATIONS

Element	WC	PYR	PC	BA	MC	ESPH1	ESPH2
Al	9.1	8.0	5.8	1.9	7.8	1.3	1.7
As	34.4	14.0	16.7	27.0	19.5	16.1	9.8
B	10.2	0.0	5.9	7.2	8.3	8.7	5.9
Ba	11.8	11.8	7.9	9.8	11.5	7.0	8.3
Be	7.2	3.1	7.7	2.9	6.2	4.8	7.0
Ca	13.5	13.4	5.7	10.7	13.5	10.1	12.2
Cd	24.7	42.4	33.3	49.7	22.9	19.8	18.2
Cl	20.0	22.0	18.7	80.6	36.3	115.4	20.6
Co	23.9	23.9	31.5	5.2	49.5	9.6	3.8
Cr	9.8	6.9	6.9	3.3	1.8	4.2	5.4
Cu	12.9	0.0	6.1	2.1	5.8	7.4	5.9
Fe	11.7	2.6	10.5	9.0	11.0	8.9	6.5
K	10.9	10.7	10.1	4.6	10.6	10.8	13.1
Mg	9.4	20.2	5.6	4.7	2.4	2.1	5.5
Mn	29.4	5.5	10.7	12.9	9.5	12.6	10.9
Na	10.1	5.9	8.4	3.2	5.4	6.2	6.1
Ni	27.5	0.0	5.6	5.2	5.9	5.2	5.6
Pb	11.4	2.0	9.3	20.1	6.6	9.1	11.5
S	10.9	0.0	8.9	33.4	14.1	9.3	28.1
Sb	21.6	20.8	59.4	19.4	25.0	26.7	13.5
Se	3.7	19.3	11.8	38.7	28.3	23.2	15.5
Si	10.3	14.4	9.5	3.0	4.4	4.4	3.5
Ti	7.6	14.2	8.1	2.5	3.5	1.5	3.0
V	7.1	0.9	5.4	1.2	5.0	4.5	4.9
Zn	11.0	3.5	9.7	51.2	13.6	11.3	22.7

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Appendix A

DESCRIPTION OF SAMPLING TRAINS

TRAIN 1 - TOTAL PARTICULATE

A schematic of this train is depicted in Figure A-1. Basically, this train is operated in the same manner as the EPA method 5 train. It traverses the gas stream and samples isokinetically. In this, as well as all other trains, 3.5-inch filter holders were used; and because of delay in the delivery of filter substrates from the vendor, Gelman AE-type filters were used instead of the intended Spectro Grade filters.

Simultaneous measurements of total particulate concentrations were carried out at the inlet and outlet of the ESP. One sampling run of 1-4 hours was made each day at each of these locations. A total of eight samples was taken at each location for the entire study.

TRAIN 2 - VAPOR-PHASE TRACE ELEMENTS

Figure A-2 shows a schematic of this train, which also served as a backup for the Hg train. This train was run under two separate methods. One method duplicated the SASS train reagents for collecting a trace element sample but at a much lower sampling rate. One test at each test plane was conducted with this test method. The remaining tests were conducted using the following procedure. In contrast to train 1, train 2 operated at a proportional flow rate and at a fixed point in the flue duct. The K_2CO_3 solution was used to collect Se, HCl, and HF, as well as to neutralize SO_2. The KOH solution was used to capture Sb and As, and also to scrub-out SO_2. The strong oxidizing solutions containing mixtures of H_2O_2, HNO_3, and $AgNO_3$ served to absorb Sb and As as well as the remaining elements listed above. The lower ends of the bubbler tubes in impingers 1, 2, and 3 were made of fritted glass with pore size of 100 μm to increase the gas-liquid contact and to enhance the collection efficiencies of the impingers.

During the sampling, the strengths of the K_2CO_3 in impinger 1 and of the H_2O_2 solutions in impingers 5 and 6 were checked by running parallel sampling with identical impingers containing K_2CO_3 and mixtures of H_2O_2, HNO_3, and $AgNO_3$, respectively. The strength of K_2CO_3 was determined by titration against H_2SO_4 to the phenolphthalein end point, and that of H_2O_2 by titration against $KMnO_4$. The absorbing solutions were replenished whenever necessary to maintain at least a 50-percent excess.

Sampling was done simultaneously at the inlet and outlet of the ESP. Preliminary studies indicated there were small concentrations of trace elements present in the gases. The original plans for collecting 4-hour samples in the morning and the afternoon were abandoned in favor of running the trains continuously for four or five days. A total of two samples was collected at the inlet and outlet of the ESP, respectively.

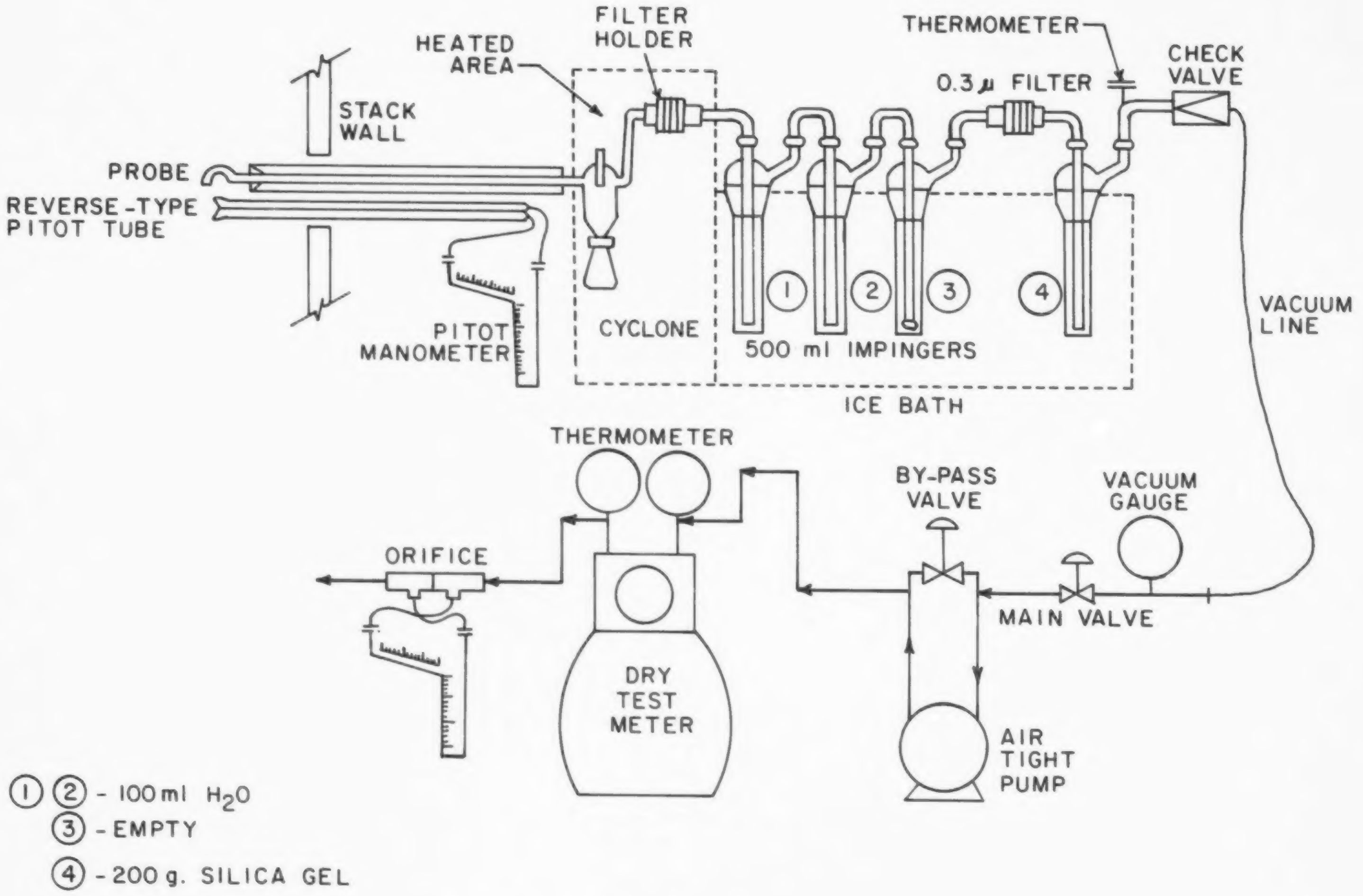
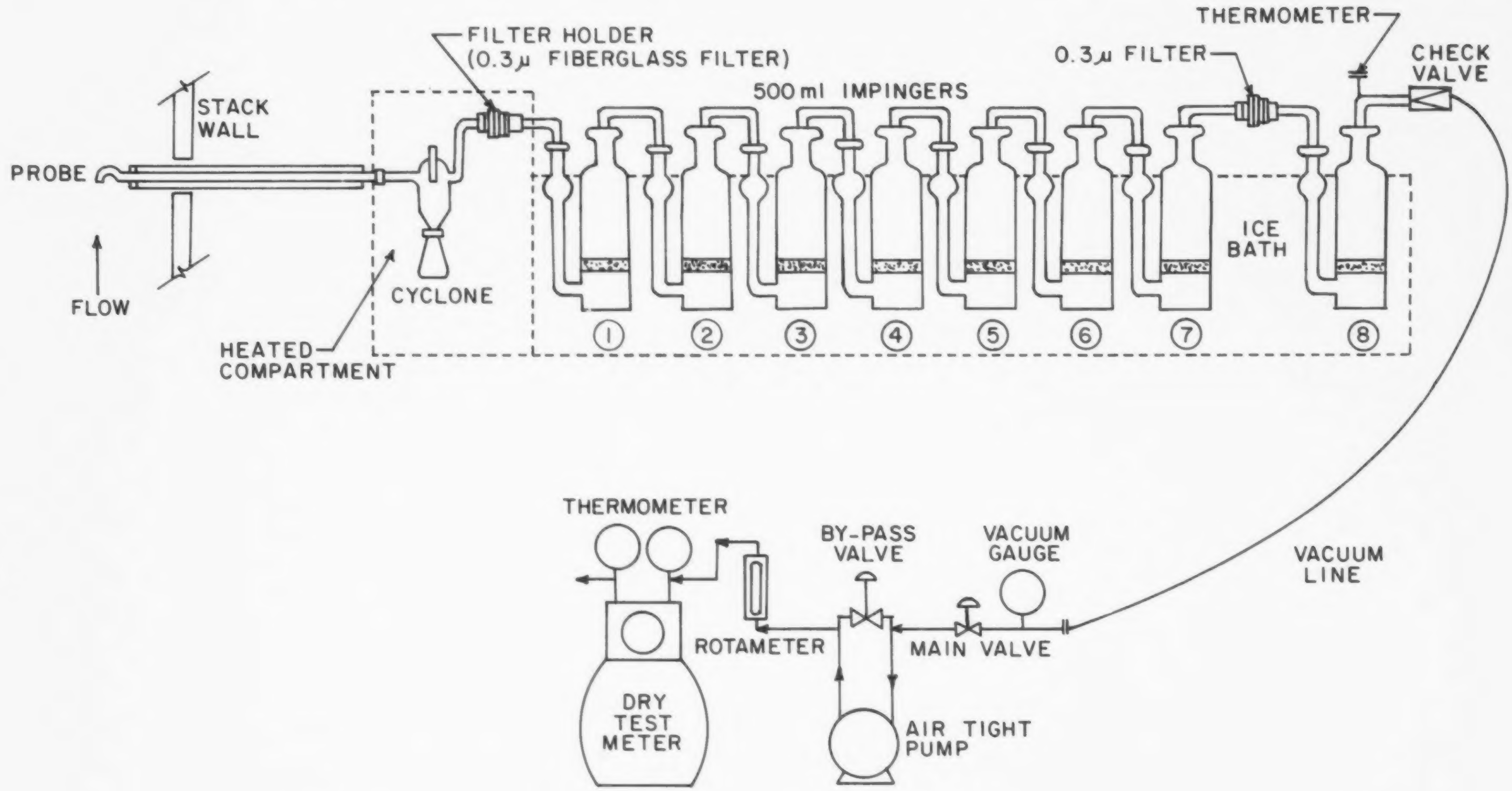

STACK WALL
HEATED AREA
FILTER HOLDER
THERMOMETER
CHECK VALVE
0.3µ FILTER
PROBE
REVERSE-TYPE PITOT TUBE
1
2
3
4
VACUUM LINE
PITOT MANOMETER
CYCLONE
500 ml IMPINGERS
ICE BATH
THERMOMETER
BY-PASS VALVE
VACUUM GAUGE
ORIFICE
MAIN VALVE
DRY TEST METER
AIR TIGHT PUMP
① ② - 100 ml H_2O
③ - EMPTY
④ - 200 g. SILICA GEL

Figure A-1. Total particulate train


FILTER HOLDER
(0.3µ FIBERGLASS FILTER)
THERMOMETER
0.3µ FILTER
CHECK VALVE
500 ml IMPINGERS
STACK WALL
PROBE
FLOW
CYCLONE
HEATED COMPARTMENT
ICE BATH
①
②
③
④
⑤
⑥
⑦
⑧
THERMOMETER
BY-PASS VALVE
VACUUM GAUGE
VACUUM LINE
ROTAMETER
MAIN VALVE
DRY TEST METER
AIR TIGHT PUMP

①-200 ml, 10% K_2CO_3 (WEIGHT/VOLUME)
②③-200 ml, 1M KOH
④⑦-EMPTY
⑤⑥-250 ml, ($2MH_2O_2 + 0.2MHNO_3 + 0.02MAgNO_3$)

Figure A-2. Vapor-phase, trace element train

TRAIN 3 - MERCURY/BACKUP VAPOR-PHASE TRACE ELEMENTS

This train is shown schematically in Figure A-3. The strong oxidizing solutions of $KMnO_4$ were effective absorbers for Hg. Impinger 1 is identical to impinger 1 used in train 2. Simultaneous sampling was done at the inlet and outlet of the ESP. Two runs were made each day: one in the morning and one in the afternoon. A total of eight samples was collected at each of the two sampling locations.

Three separate solutions were retained for samples collected from this train. The first was the catch in the K_2CO_3 solution from impinger 1. The second was the combined catch from the $KMnO_4$ and HNO_3 solutions in impingers 2-5. The third was the solution obtained from rinsing impingers 2-5 with 10-percent oxalic acid solution.

BRINK CASCADE IMPACTOR

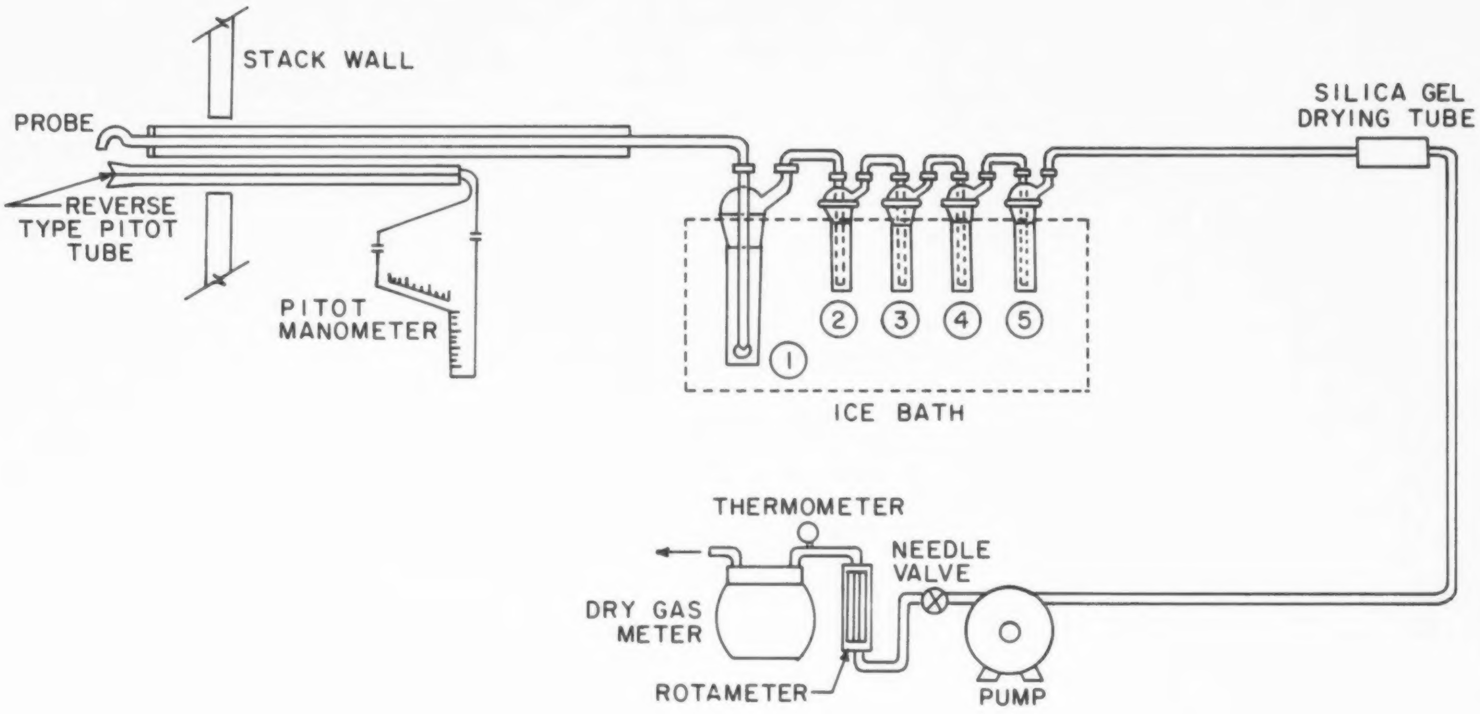
Figure A-4 is a schematic illustration of the BSM11, 5-stage Brink impactor for particle size classification. Because of its lower gas sampling flow rate and larger capacity, the Brink impactor was used at the ESP inlet. Teflon and aluminum substrates were used with the stages, but Teflon was found to be a very poor collection substrate during preliminary tests. Final tests were conducted using aluminum substrates.

A run of 2.5 to 7 minutes was made with the impactor in the morning and again in the afternoon during each sampling day. The impactor was inserted to a depth of five feet into the duct, and the sampling rate was adjusted to achieve isokinetic sampling from an experimentally predetermined flue gas velocity at that point.

The impactor was preheated in the flue for 30 minutes to attain thermal equilibrium before commencement of sampling.

ANDERSEN CASCADE IMPACTOR

Figure A-5 shows a schematic diagram of the Andersen system. Because of its higher volume flow rate, this impactor was used at the ESP outlet to obtain size distribution information. Fiberglass filters were used as substrate. The sampling procedure used was identical to that followed for the Brink Cascade Impactor.


STACK WALL
PROBE
REVERSE TYPE PITOT TUBE
PITOT MANOMETER
①
②
③
④
⑤
ICE BATH
SILICA GEL DRYING TUBE
THERMOMETER
NEEDLE VALVE
DRY GAS METER
ROTAMETER
PUMP

① - 200 ml, 10% K_2CO_3 (WEIGHT/VOLUME)
②③④ - 20 ml, (3% $KMnO_4$ + 14.3% HNO_3)
⑤ - EMPTY

Figure A-3. Mercury train/back-up for vapor-phase trace elements

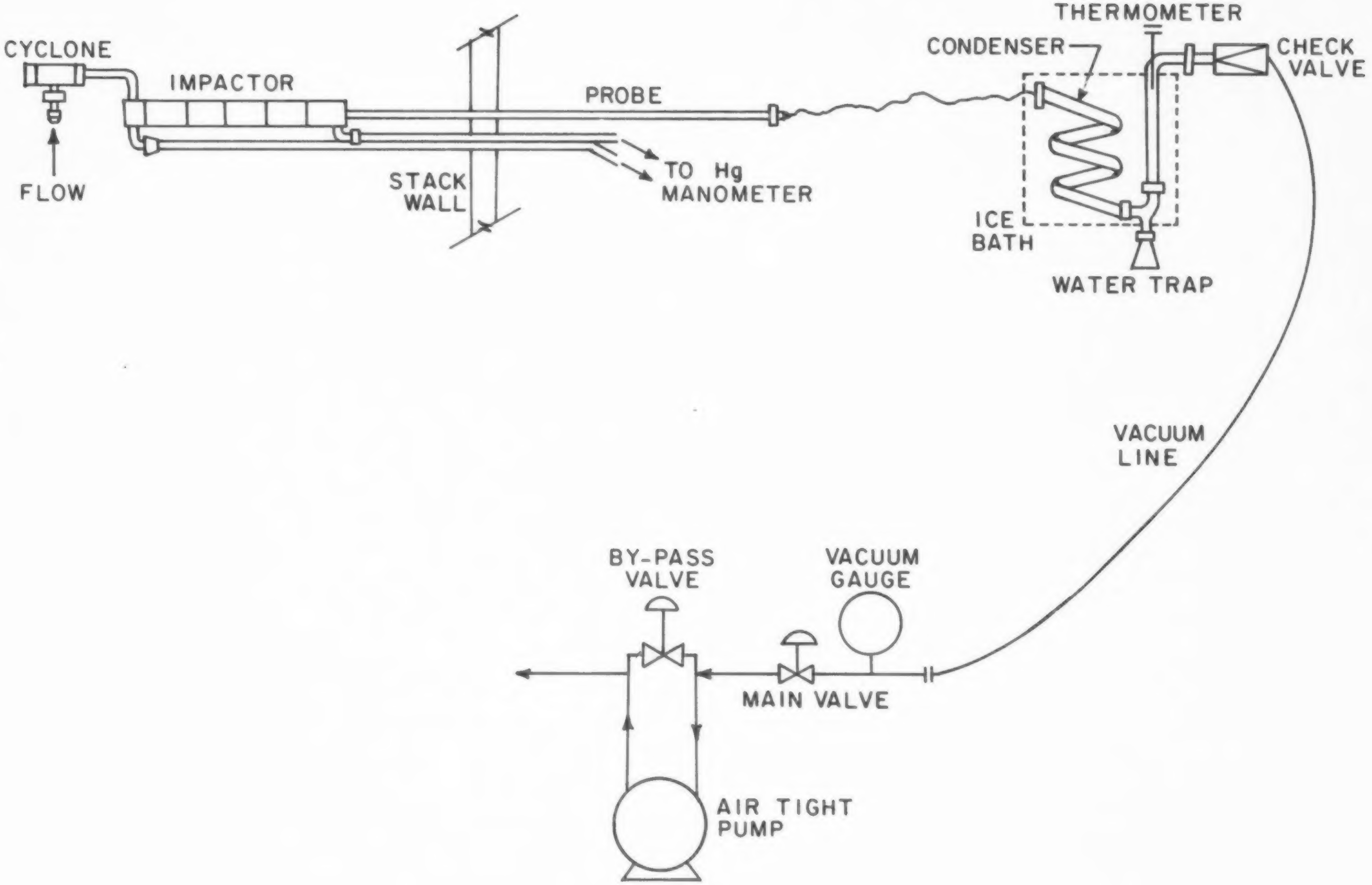

CYCLONE
FLOW
IMPACTOR
STACK WALL
PROBE
TO Hg MANOMETER
CONDENSER
THERMOMETER
CHECK VALVE
ICE BATH
WATER TRAP
VACUUM LINE
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
AIR TIGHT PUMP

Figure A-4. Brink cascade impactor sampling train

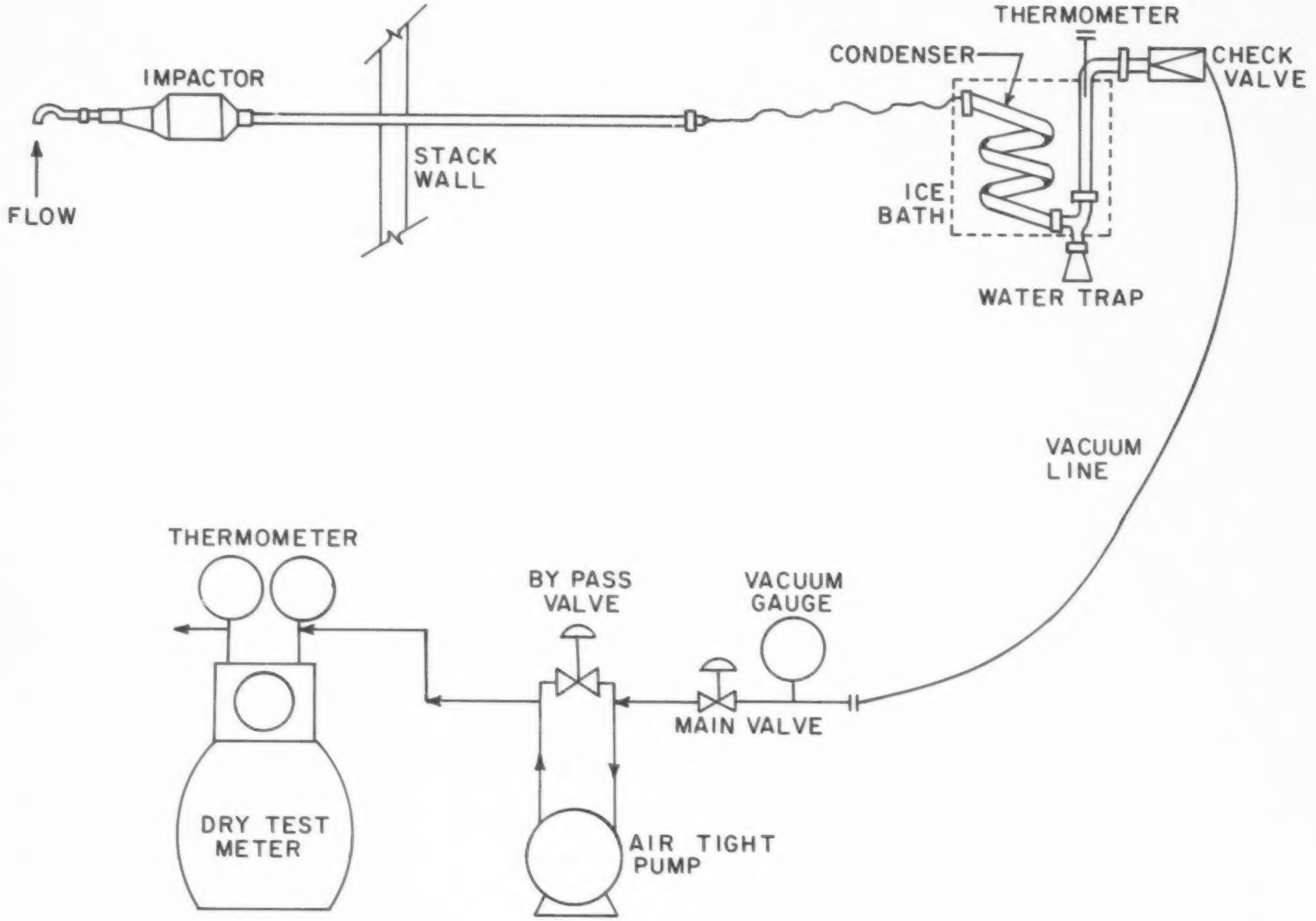

THERMOMETER
CONDENSER
CHECK VALVE
IMPACTOR
STACK WALL
FLOW
ICE BATH
WATER TRAP
VACUUM LINE
THERMOMETER
BY PASS VALVE
VACUUM GAUGE
MAIN VALVE
DRY TEST METER
AIR TIGHT PUMP

Figure A-5. Andersen impactor sampling train

Appendix B

METHODS OF CHEMICAL ANALYSIS

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METHODS OF CHEMICAL ANALYSIS

Table B-I gives the nine analytical methods that were used to determine the 27 trace elements in the various gaseous and particulate samples collected by the different sampling trains. Also, Table B-I gives methods for the coal and electrostatic precipitator ash samples. This table also gives the sample size required for each sample type. Figures B-1-11 display the flow scheme for the analytical procedures used to determine trace elements in coal, electrostatic precipitator ash, impinger water from the total particulate train, gases from the vapor phase train, ash from the total particulate train, gases from mercury vapor phase train, ash from the SASS train, XAD-2 resin from the SASS train, gases from the SASS train, ash from the Brink impactor, and ash from the Andersen impactor.

Coal, XAD-2 resin, and ash samples were prepared for analysis by digestion with acids (HF-Aqua Regia or HF-$HClO_4$), bases (lithium metaborate, Eschka's mixture, or Na_2CO_3-$NaHCO_3$), and/or combustion (oxygen bomb, induction furnace, or ignition). The solutions that resulted from digestion were then assayed for the elements by procedures given in Table B-I and processed by flow diagrams in Figures B-1, B-2, B-4, B-7, B-8, B-10, and B-11.

Absolute ethanol was used to dislodge very small ash samples from their substrates (e.g., filters, pans, and beakers) so that sufficient material could be composited for micro-chemical analysis. This technique was used to determine 26 trace elements in the small ash samples from the total particulate train, the SASS train, the Brink impactor, and the Andersen impactor. See Figures B-4, B-7, B-10, and B-11 to learn specific treatment.

Liquid samples (such as KOH, K_2CO_3, water, H_2O_2, H_2O_2 with $AgNO_3$, $KMnO_4$ in HNO_3, oxalic acid, persulfate with $AgNO_3$, persulfate with $AgNO_3$ containing isopropyl alcohol, and methylene chloride extract) were analyzed directly, diluted for analysis, evaporated, acidified, and/or oxidized for chemical analysis. See Figures B-3, B-5, B-6, and B-9 to learn specific treatment.

1 Analytical Procedures for Trace Elements in Coal

1.a Preparation of Coal Samples

The air-dry moisture was first determined for the coal samples by weighing the sample, then drying in a forced air oven at approximately 40°C for 16 hours according to ASTM Standard D3302 (1). The samples were reweighed and the percent air-dry moisture calculated. The air-dried coal sample was then pulverized in a Raymond Mill to less than 60 mesh according to ASTM Standard D2013 (1). From the air-dried, pulverized sample laboratory, moisture was determined on all coal samples by drying in a special furnace at 110°C according to ASTM Standard D3173 (1).

TABLE B-I

METHODS OF CHEMICAL ANALYSIS OF TRACE ELEMENTS

			Total Particulate Train		Gases from Vapor Phase Train		Mercury Vapor Phase Train		
Instrumental Method	Coal	ESP Ash	Water Impinger	Ash	K_2CO_3 or KOH	H_2O_2 with $AgNO_3$	K_2CO_3	$KMnO_4$ in HNO_3	Oxalic Acid Rinse
Sample Size Required	10 Grams	3.5 Grams	200 ML	10 MG	200 ML	200 ML	100 ML	10 ML	75 ML
Inductively Coupled Argon Plasma Atomic Emission Spectroscopy	Be, B, Cr, Cu, Fe, Pb, Ni, V, Zn, Ba, Ca, Mg, Mn, Si, Ti	Be, B, Cr, Cu, Fe, Pb, Ni, V, Zn, Ba, Ca, Mg, Mn, Si, Ti	Al, Ba, Be, Ca, Cu, Fe, Mg, Mn, Ti, V, Zn, B, Si, Na	Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn	Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Na, Pb, Ti, V, Zn, Si, B	Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na	-	-	-
Atomic Absorption	Cd, Al, Co, Na, K, As, Se, Sb, Hg	Cd, Al, Co, Na, K, As, Se, Sb, Hg	K, Cd, Pb, Cr, Co, Ni, Se, As, Sb	Co, As, Se, Sb, Hg	Co, As, Sb, Se	Co, As, Sb, Se	Hg	Hg	Hg
Gravimetry	-	-	-	-	-	Cl	-	-	-
Potentiometric Titration	Cl	-	Cl	-	Cl	-	-	-	-
Ion Chromatography	-	Cl	-	Cl, F, S	-	-	-	-	-
Ion Selective Electrode	F	F	F	-	F	F	-	-	-
Induction Furnace	S	S	-	-	-	-	-	-	-
Stripping Voltammetry	-	-	-	Cd	-	-	-	-	-
Turbidimetry	-	-	S	-	S	S	-	-	-

TABLE B-I (CONTINUED)

METHODS OF CHEMICAL ANALYSIS

	SASS Train						
Instrumental Method	Ash	XAD-2 Resin	H_2O_2 Impinger	Persulfate with $AgNO_3$ Impinger	Persulfate with $AgNO_3$ and Isopropyl Alcohol	Aqueous Condensate	CH_2Cl_2 Extract
Sample Size Required	10 MG	10 Grams	200 ML	200 ML	200 ML	200 ML	10 MG
Inductively Coupled Argon Plasma Atomic Emission Spectroscopy	Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn,	Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn	Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na	Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na	Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na	Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na	Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn
Atomic Absorption	Co, As, Se, Sb, Hg	Co, Sb, As, Se, Hg	Co, As, Sb, Se	Co, As, Sb, Se	Co, As, Se, Sb	Co, As, Se, Sb	Co, As, Se, Sb, Hg
Gravimetry	-	-	-	Cl	Cl	-	-
Potentiometric Titration	-	-	Cl	-	-	Cl	-
Ion Chromatography	Cl, F, S	Cl, F	-	-	-	-	Cl, F, S
Ion Selective Electrode	-	-	F	F	F	F	-
Induction Furnace	-	S	-	-	-	-	-
Stripping Voltammetry	Cd	Cd	-	-	-	-	Cd
Turbidimetry	-	-	S	S	S	S	-

TABLE B-I (CONTINUED)

METHODS OF CHEMICAL ANALYSIS

Instrumental Method	Ash from Brink Impactor	Ash from Andersen Impactor
Sample Size Required	1 MG	10 MG
Inductively Coupled Argon Plasma Atomic Emission Spectroscopy	Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn	Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn
Atomic Absorption	Co, As, Se, Sb, Hg	Co, As, Se, Sb, Hg
Gravimetry	-	-
Potentiometric Titration	-	-
Ion Chromatography	Cl, F, S	Cl, F, S
Ion Selective Electrode	-	-
Induction Furnace	-	-
Stripping Voltammetry	Cd	Cd
Turbidimetry	-	-

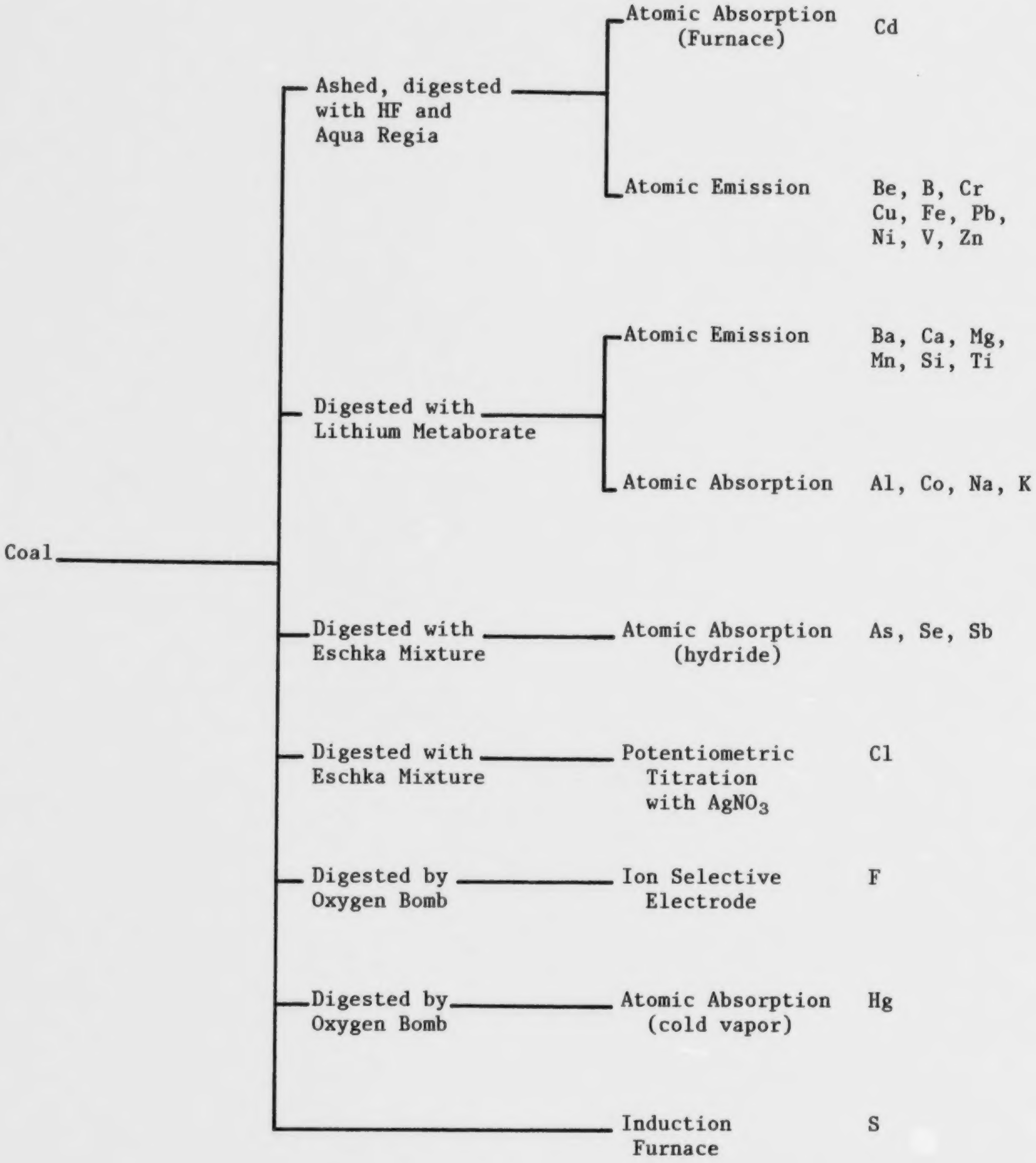
Coal
Ashed, digested with HF and Aqua Regia
Atomic Absorption (Furnace)
Cd
Atomic Emission
Be, B, Cr Cu, Fe, Pb, Ni, V, Zn
Digested with Lithium Metaborate
Atomic Emission
Ba, Ca, Mg, Mn, Si, Ti
Atomic Absorption
Al, Co, Na, K
Digested with Eschka Mixture
Atomic Absorption (hydride)
As, Se, Sb
Digested with Eschka Mixture
Potentiometric Titration with $AgNO_3$
Cl
Digested by Oxygen Bomb
Ion Selective Electrode
F
Digested by Oxygen Bomb
Atomic Absorption (cold vapor)
Hg
Induction Furnace
S

Figure B-1. Analytical procedures for trace element analysis in coal.

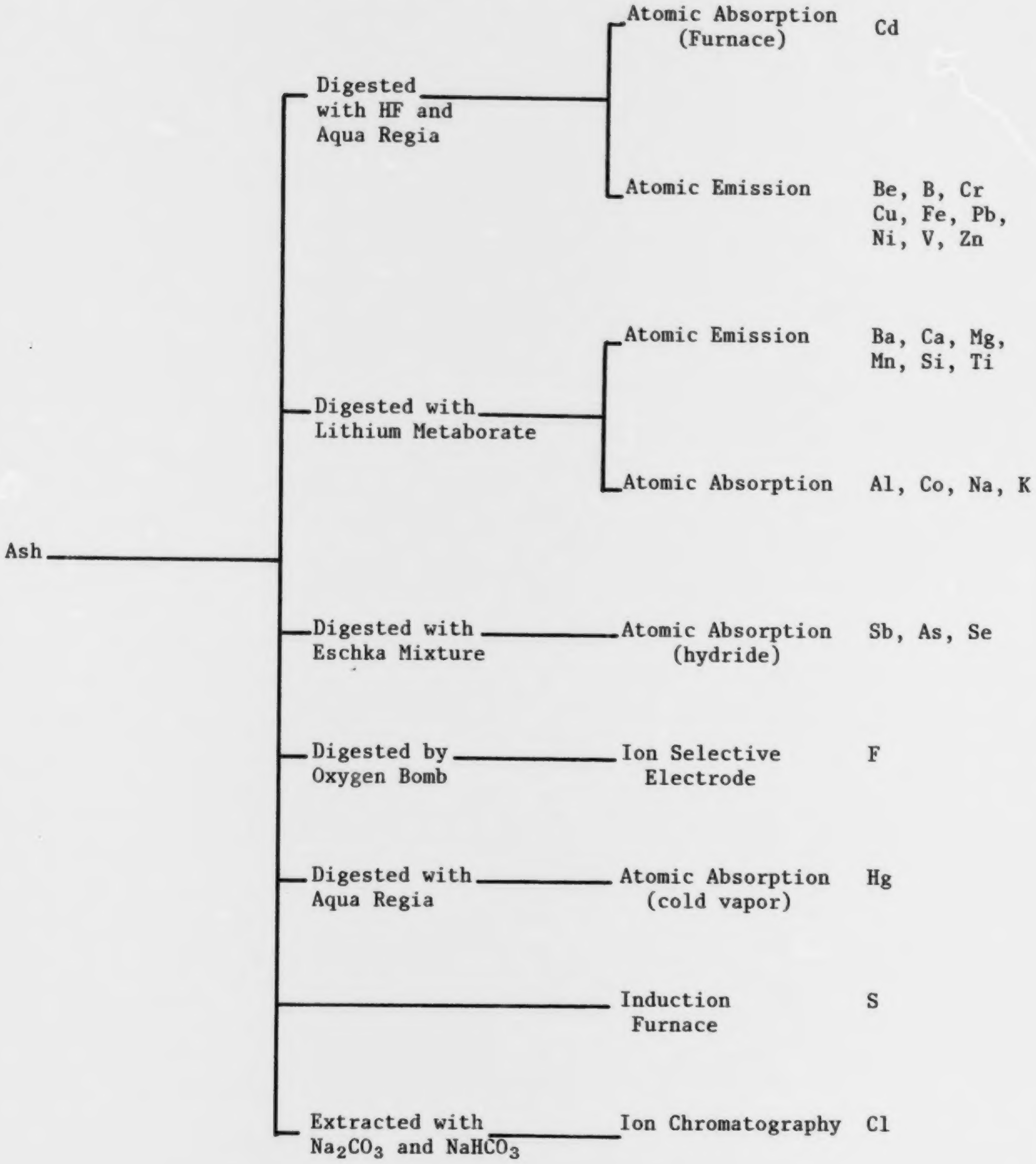
Atomic Absorption (Furnace)
Cd
Digested with HF and Aqua Regia
Atomic Emission
Be, B, Cr Cu, Fe, Pb, Ni, V, Zn
Atomic Emission
Ba, Ca, Mg, Mn, Si, Ti
Digested with Lithium Metaborate
Atomic Absorption
Al, Co, Na, K
Ash
Digested with Eschka Mixture
Atomic Absorption (hydride)
Sb, As, Se
Digested by Oxygen Bomb
Ion Selective Electrode
F
Digested with Aqua Regia
Atomic Absorption (cold vapor)
Hg
Induction Furnace
S
Extracted with Na2CO3 and NaHCO3
Ion Chromatography
Cl

Figure B-2. Analytical procedures for trace elements in electrostatic precipitator ash.

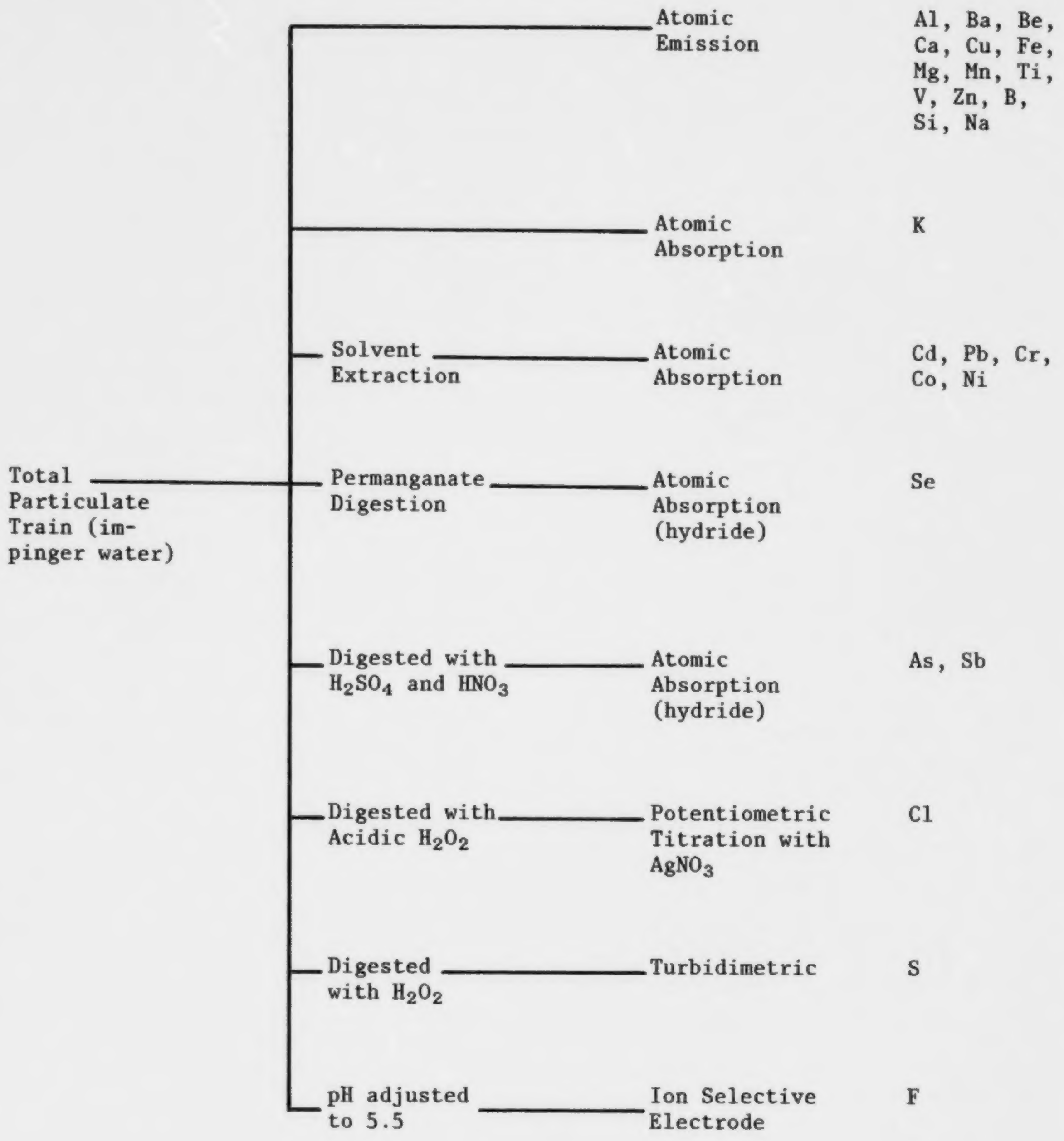
Total Particulate Train (impinger water)
Atomic Emission
Al, Ba, Be, Ca, Cu, Fe, Mg, Mn, Ti, V, Zn, B, Si, Na
Atomic Absorption
K
Solvent Extraction
Atomic Absorption
Cd, Pb, Cr, Co, Ni
Permanganate Digestion
Atomic Absorption (hydride)
Se
Digested with H_2SO_4 and HNO_3
Atomic Absorption (hydride)
As, Sb
Digested with Acidic H_2O_2
Potentiometric Titration with $AgNO_3$
Cl
Digested with H_2O_2
Turbidimetric
S
pH adjusted to 5.5
Ion Selective Electrode
F

Figure B-3. Analytical procedures for trace elements in the impinger water from the total particulate train.

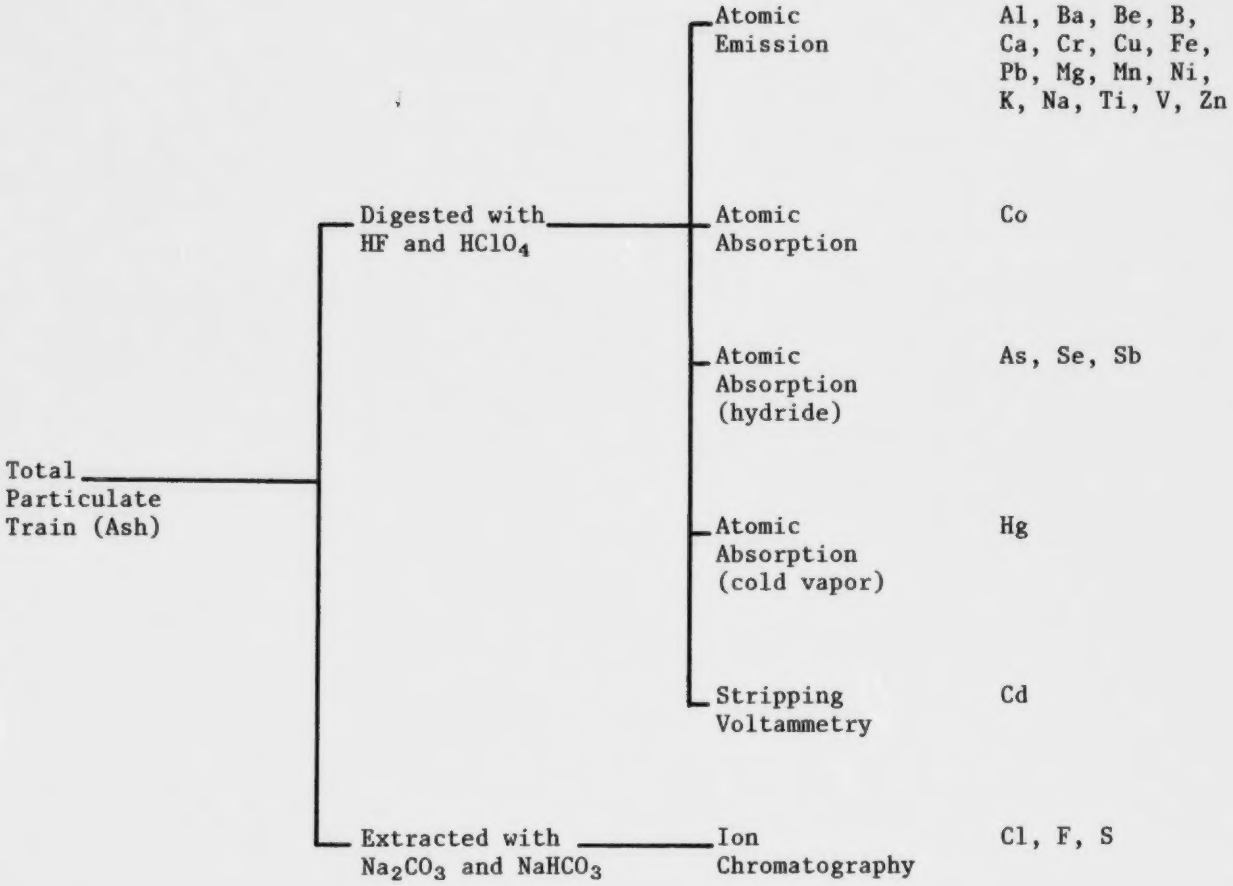
Total Particulate Train (Ash)
Digested with HF and $HClO_4$
Extracted with Na_2CO_3 and $NaHCO_3$
Atomic Emission
Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn
Atomic Absorption
Co
Atomic Absorption (hydride)
As, Se, Sb
Atomic Absorption (cold vapor)
Hg
Stripping Voltammetry
Cd
Ion Chromatography
Cl, F, S

Figure B-4. Analytical procedure for trace elements in the ash from the total particulate train.

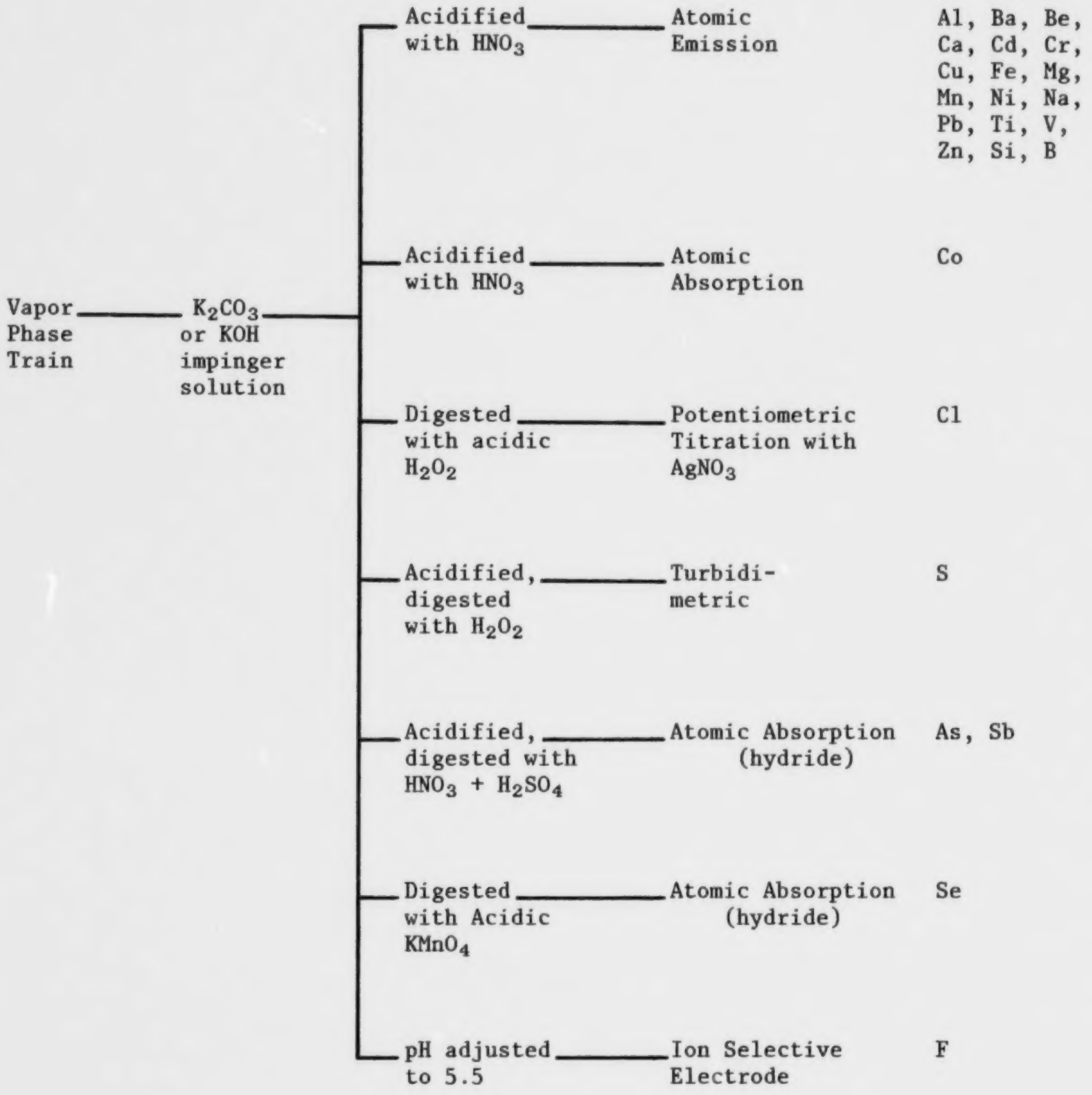
Vapor Phase Train
K_2CO_3 or KOH impinger solution
Acidified with HNO_3
Atomic Emission
Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Na, Pb, Ti, V, Zn, Si, B
Acidified with HNO_3
Atomic Absorption
Co
Digested with acidic H_2O_2
Potentiometric Titration with $AgNO_3$
Cl
Acidified, digested with H_2O_2
Turbidimetric
S
Acidified, digested with HNO_3 + H_2SO_4
Atomic Absorption (hydride)
As, Sb
Digested with Acidic $KMnO_4$
Atomic Absorption (hydride)
Se
pH adjusted to 5.5
Ion Selective Electrode
F

Figure B-5. Analytical procedures for trace elements in the gases from the vapor phase train.

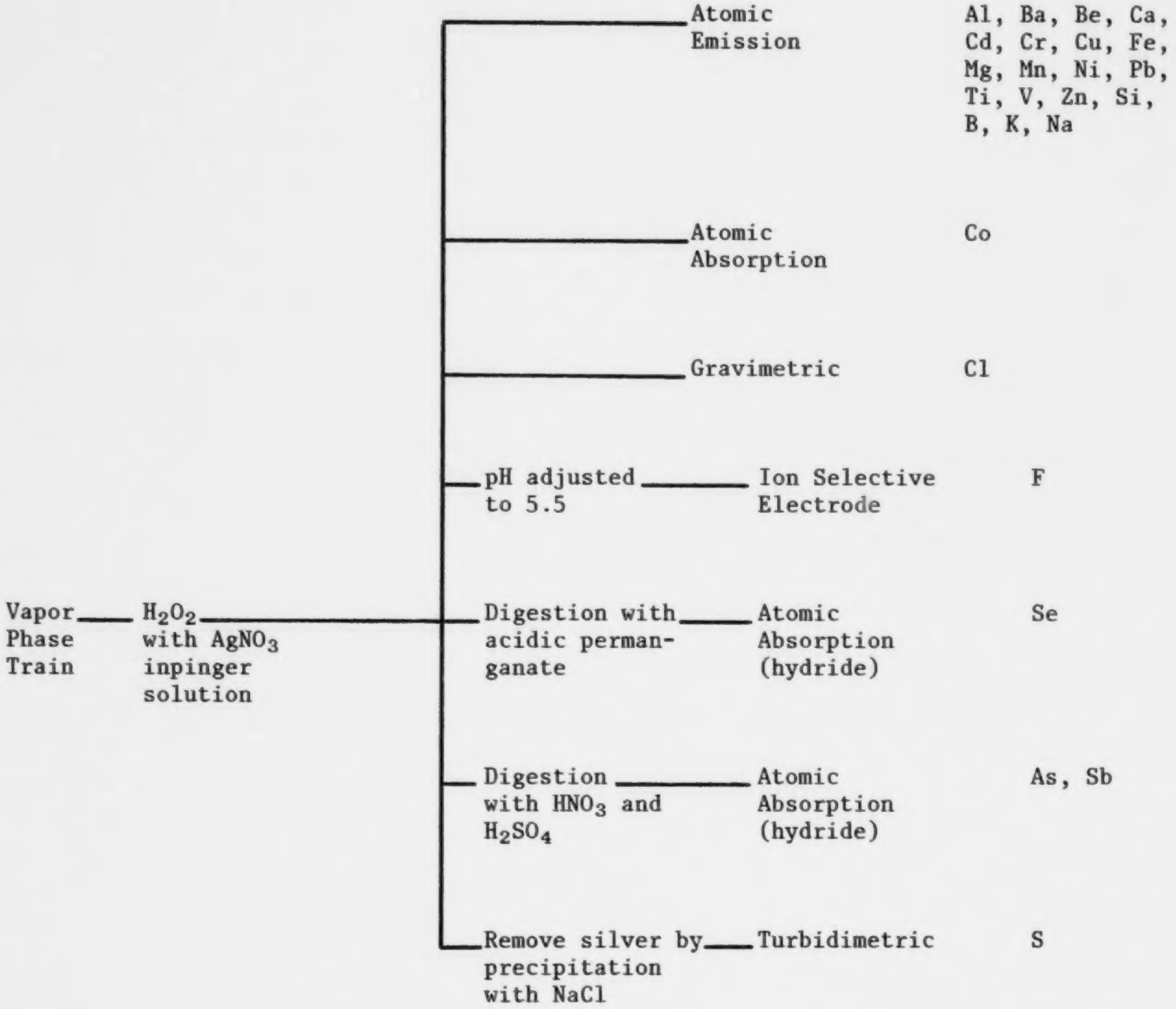
Vapor Phase Train
H_2O_2 with $AgNO_3$ inpinger solution
Atomic Emission
Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na
Atomic Absorption
Co
Gravimetric
Cl
pH adjusted to 5.5
Ion Selective Electrode
F
Digestion with acidic permanganate
Atomic Absorption (hydride)
Se
Digestion with HNO_3 and H_2SO_4
Atomic Absorption (hydride)
As, Sb
Remove silver by precipitation with NaCl
Turbidimetric
S

Figure B-5. (Continued)

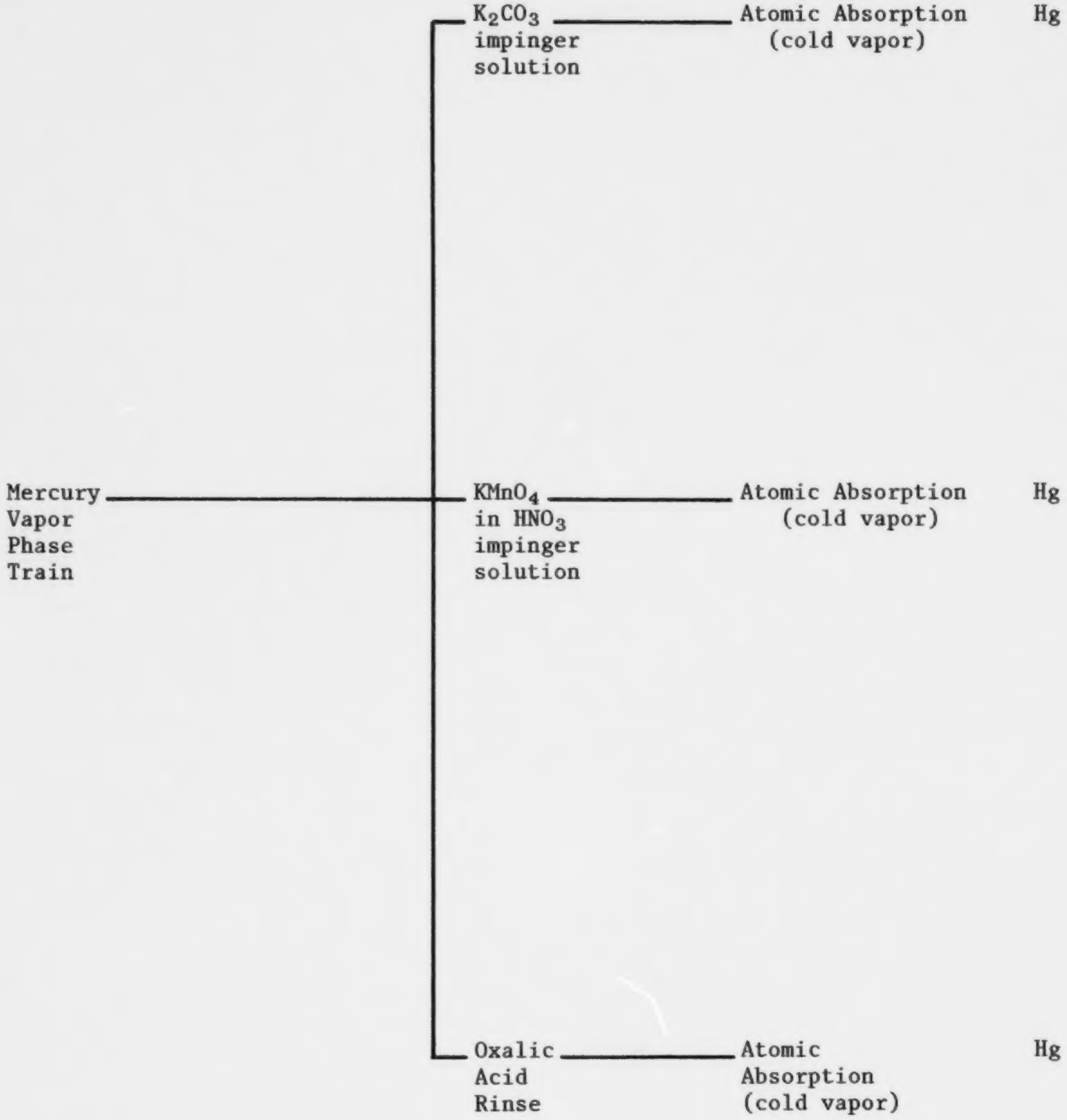
Mercury Vapor Phase Train
K_2CO_3 impinger solution
Atomic Absorption (cold vapor)
Hg
$KMnO_4$ in HNO_3 impinger solution
Atomic Absorption (cold vapor)
Hg
Oxalic Acid Rinse
Atomic Absorption (cold vapor)
Hg

Figure B-6. Analytical procedures for mercury collected by the mercury vapor phase train.

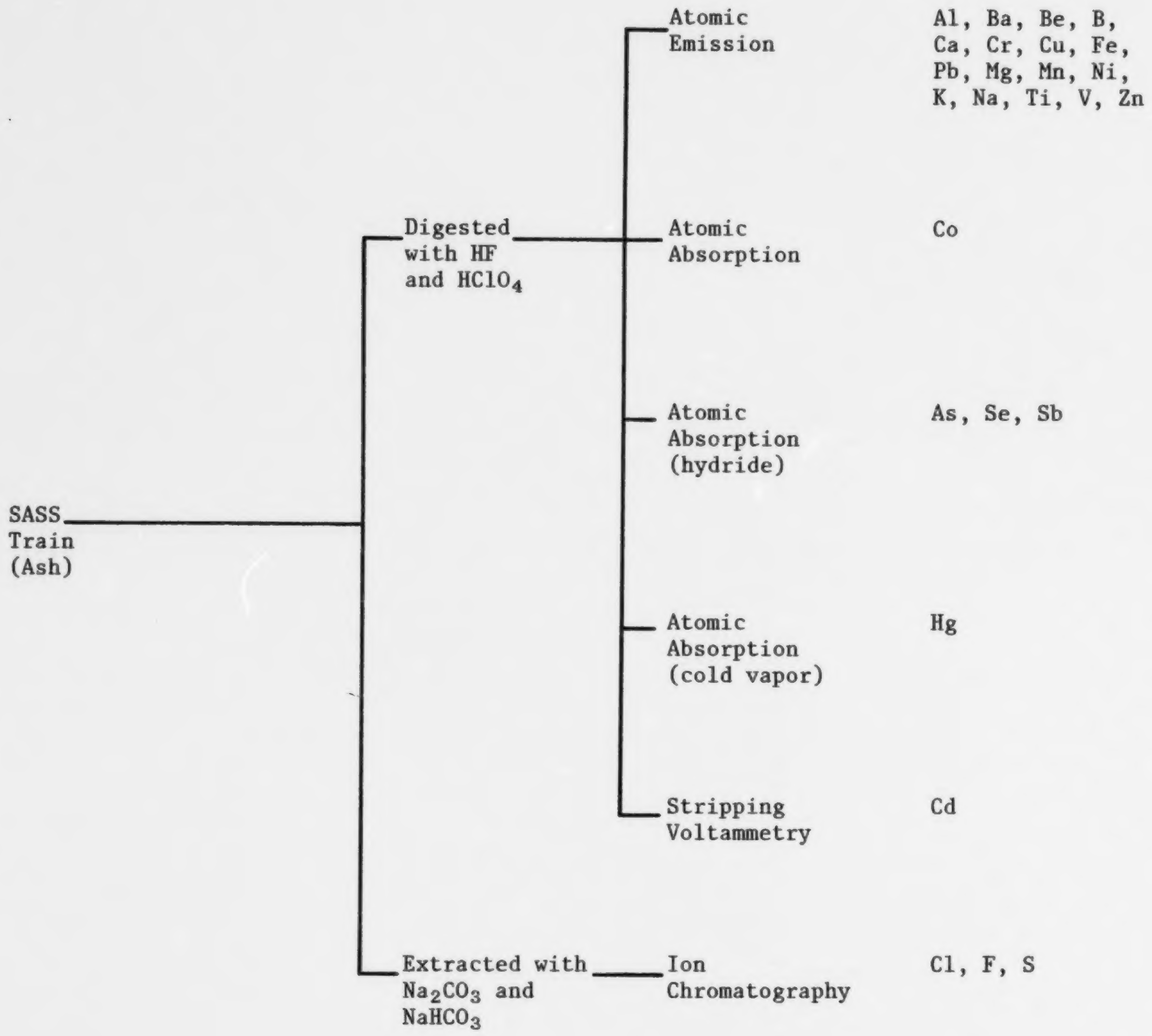
SASS Train (Ash)
Digested with HF and $HClO_4$
Extracted with Na_2CO_3 and $NaHCO_3$
Atomic Emission
Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn
Atomic Absorption
Co
Atomic Absorption (hydride)
As, Se, Sb
Atomic Absorption (cold vapor)
Hg
Stripping Voltammetry
Cd
Ion Chromatography
Cl, F, S

Figure B-7. Analytical procedures for trace elements in the ash from the SASS train.

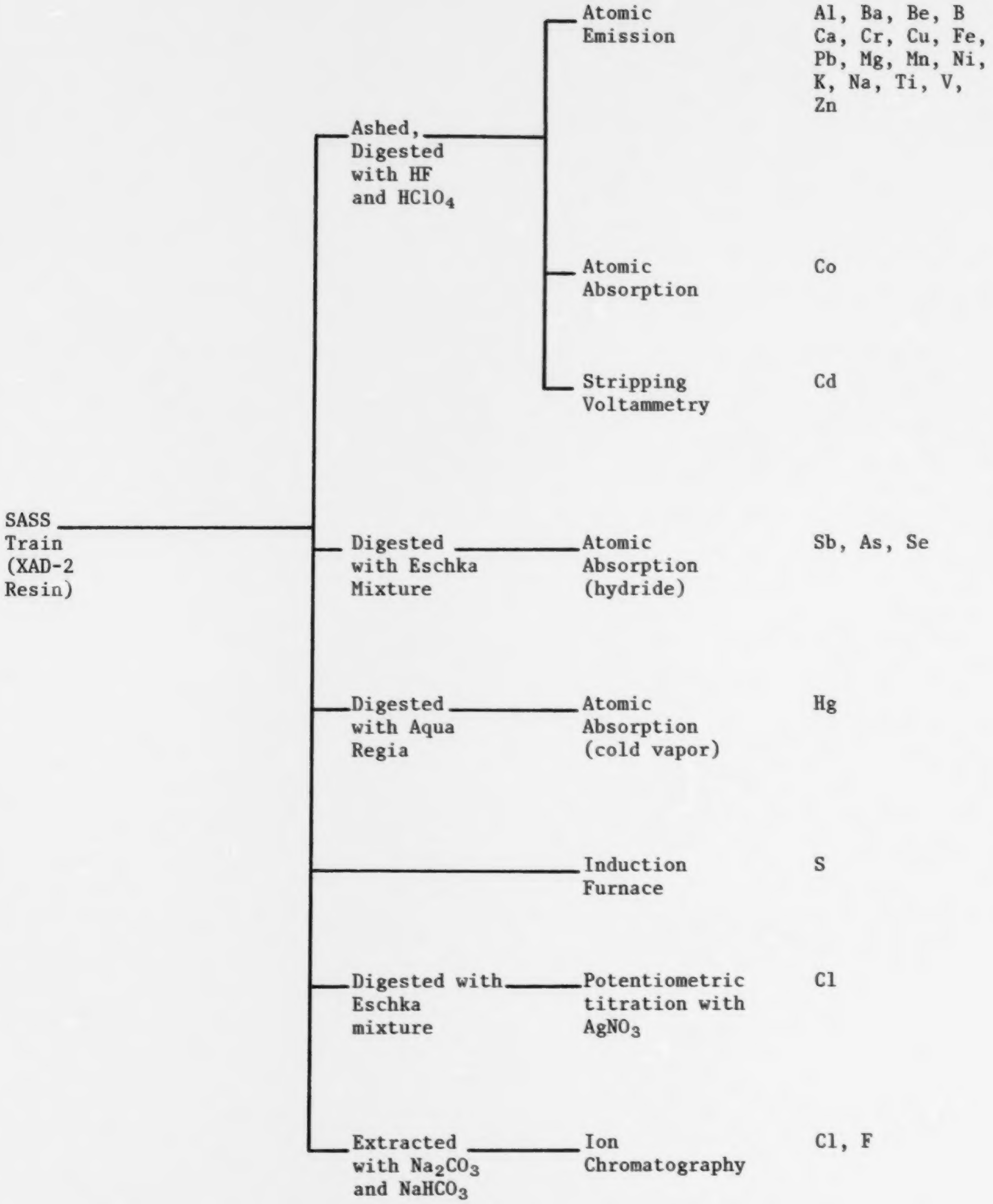
SASS Train (XAD-2 Resin)
Ashed, Digested with HF and $HClO_4$
Atomic Emission
Al, Ba, Be, B Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn
Atomic Absorption
Co
Stripping Voltammetry
Cd
Digested with Eschka Mixture
Atomic Absorption (hydride)
Sb, As, Se
Digested with Aqua Regia
Atomic Absorption (cold vapor)
Hg
Induction Furnace
S
Digested with Eschka mixture
Potentiometric titration with $AgNO_3$
Cl
Extracted with Na_2CO_3 and $NaHCO_3$
Ion Chromatography
Cl, F

Figure B-8. Analytical procedures for trace elements in the XAD-2 resin from the SASS train.

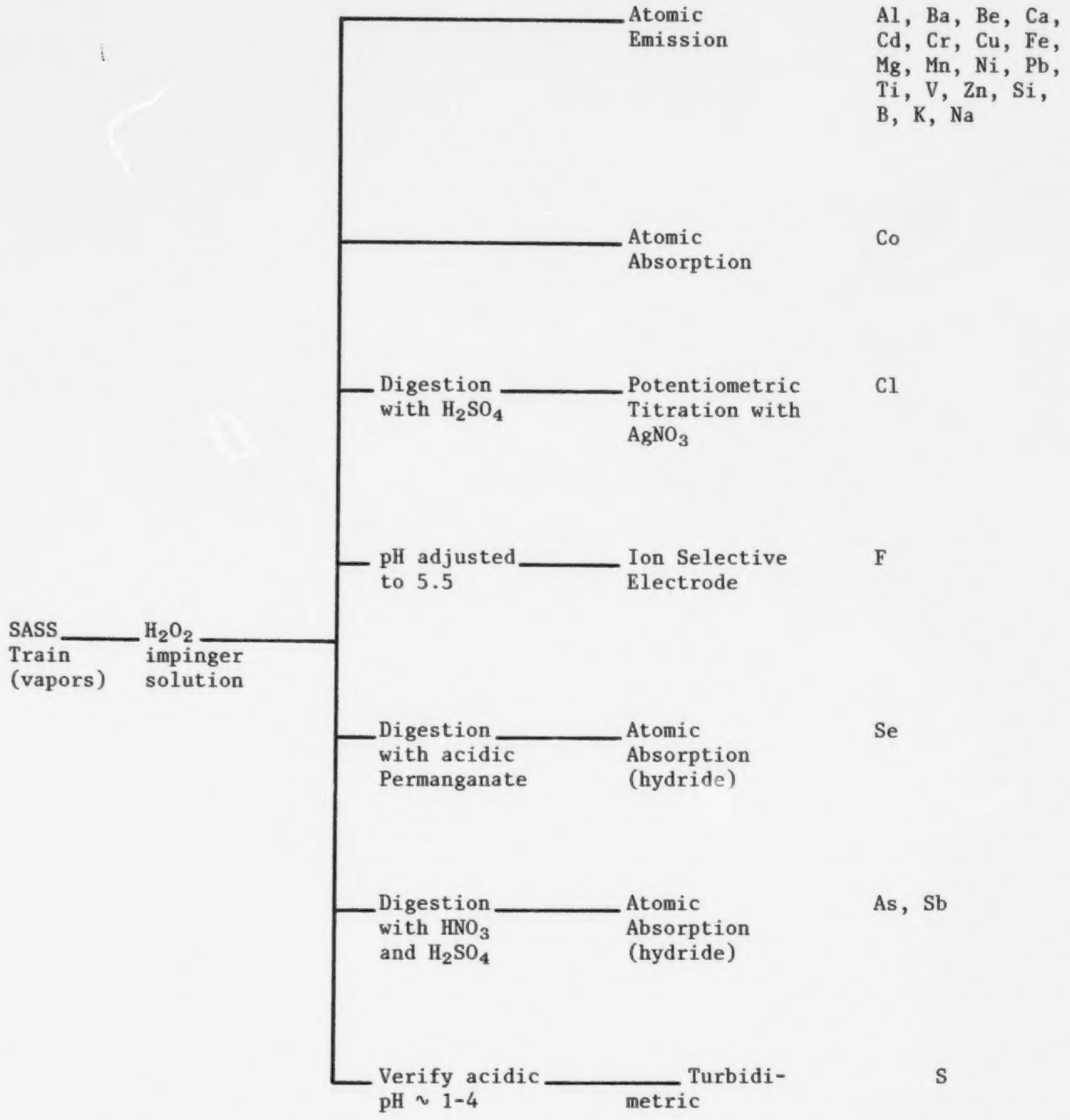
SASS Train (vapors)
H_2O_2 impinger solution
Atomic Emission
Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na
Atomic Absorption
Co
Digestion with H_2SO_4
Potentiometric Titration with $AgNO_3$
Cl
pH adjusted to 5.5
Ion Selective Electrode
F
Digestion with acidic Permanganate
Atomic Absorption (hydride)
Se
Digestion with HNO_3 and H_2SO_4
Atomic Absorption (hydride)
As, Sb
Verify acidic pH ∼ 1-4
Turbidimetric
S

Figure B-9. Analytical procedures for trace elements in gases from the SASS train.

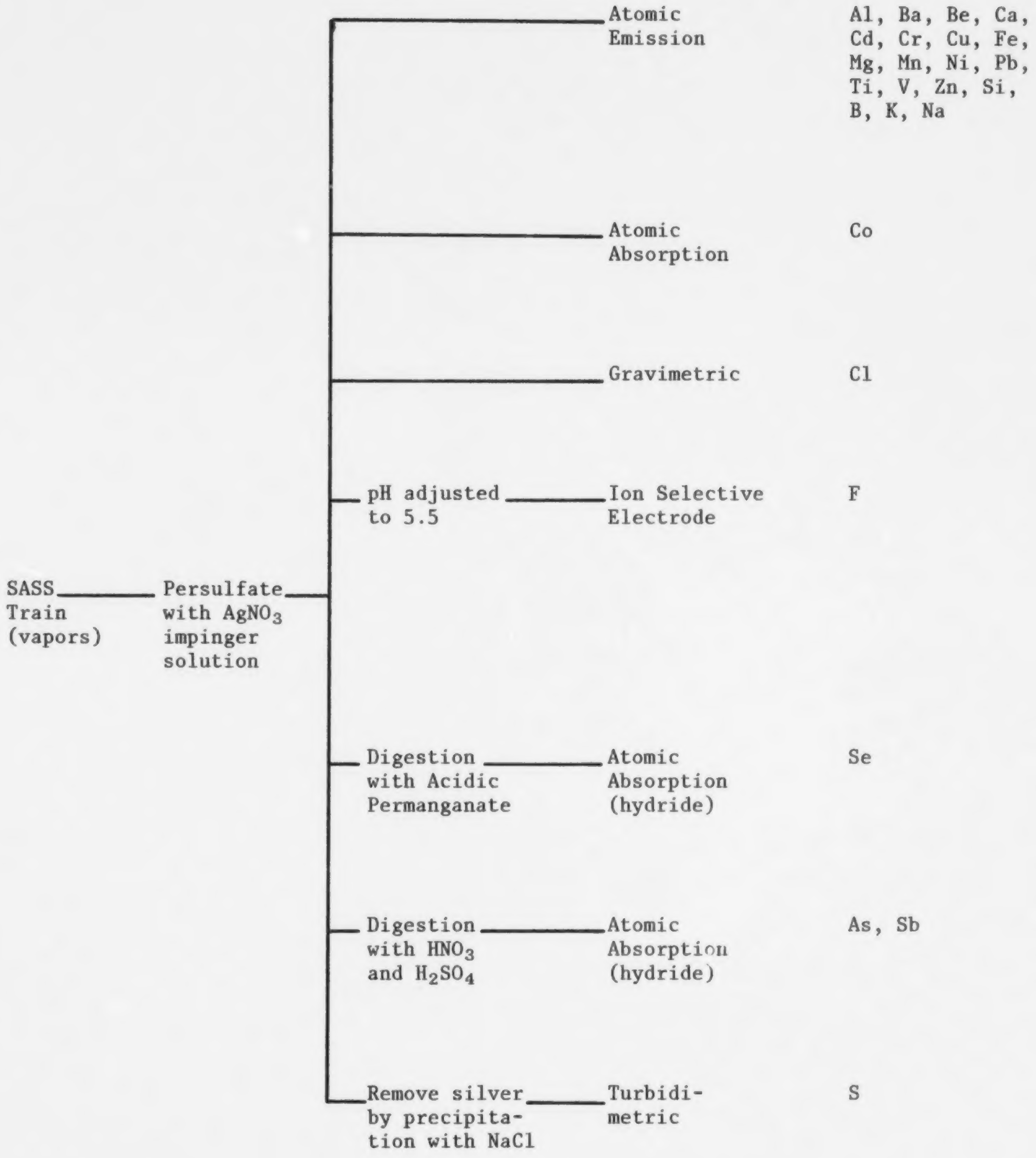
SASS Train (vapors)
Persulfate with $AgNO_3$ impinger solution
Atomic Emission
Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na
Atomic Absorption
Co
Gravimetric
Cl
pH adjusted to 5.5
Ion Selective Electrode
F
Digestion with Acidic Permanganate
Atomic Absorption (hydride)
Se
Digestion with HNO_3 and H_2SO_4
Atomic Absorption (hydride)
As, Sb
Remove silver by precipitation with NaCl
Turbidimetric
S

Figure B-9. (Continued)

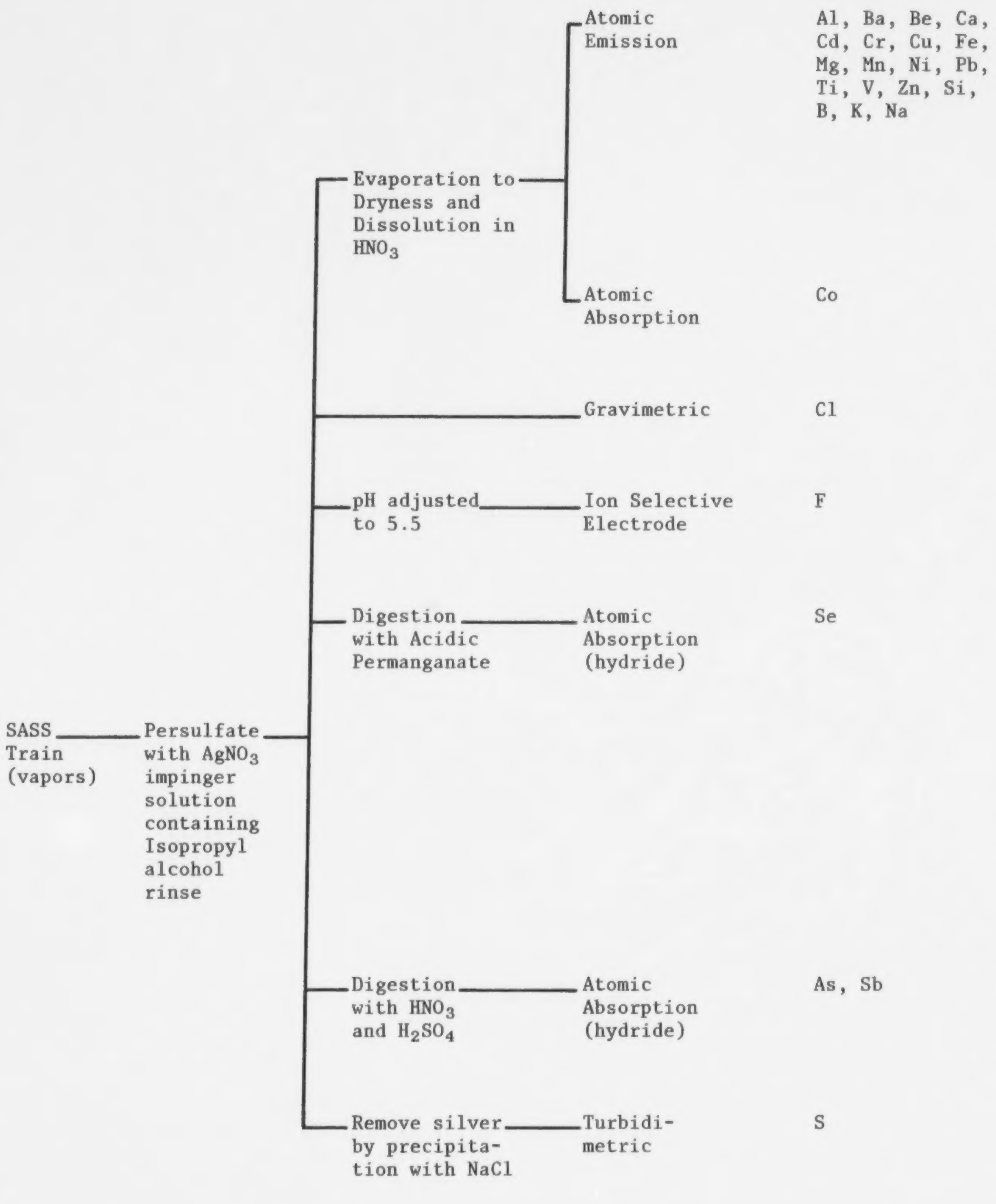
SASS Train (vapors)
Persulfate with $AgNO_3$ impinger solution containing Isopropyl alcohol rinse
Evaporation to Dryness and Dissolution in HNO_3
Atomic Emission
Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na
Atomic Absorption
Co
Gravimetric
Cl
pH adjusted to 5.5
Ion Selective Electrode
F
Digestion with Acidic Permanganate
Atomic Absorption (hydride)
Se
Digestion with HNO_3 and H_2SO_4
Atomic Absorption (hydride)
As, Sb
Remove silver by precipitation with NaCl
Turbidimetric
S

Figure B-9. (Continued)

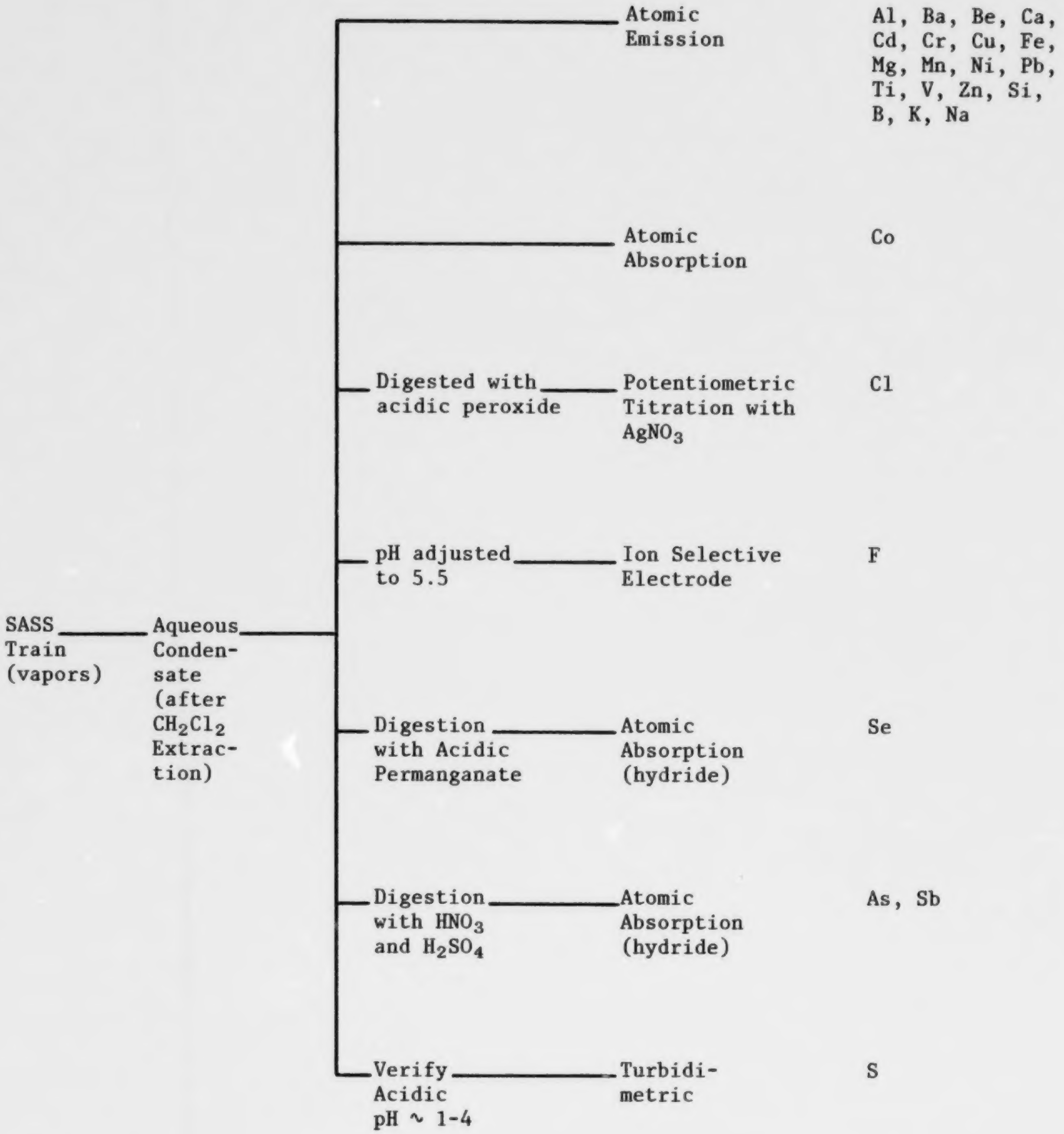
SASS Train (vapors)
Aqueous Condensate (after CH_2Cl_2 Extraction)
Atomic Emission
Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, Na
Atomic Absorption
Co
Digested with acidic peroxide
Potentiometric Titration with $AgNO_3$
Cl
pH adjusted to 5.5
Ion Selective Electrode
F
Digestion with Acidic Permanganate
Atomic Absorption (hydride)
Se
Digestion with HNO_3 and H_2SO_4
Atomic Absorption (hydride)
As, Sb
Verify Acidic pH ∼ 1-4
Turbidimetric
S

Figure B-9. (Continued)

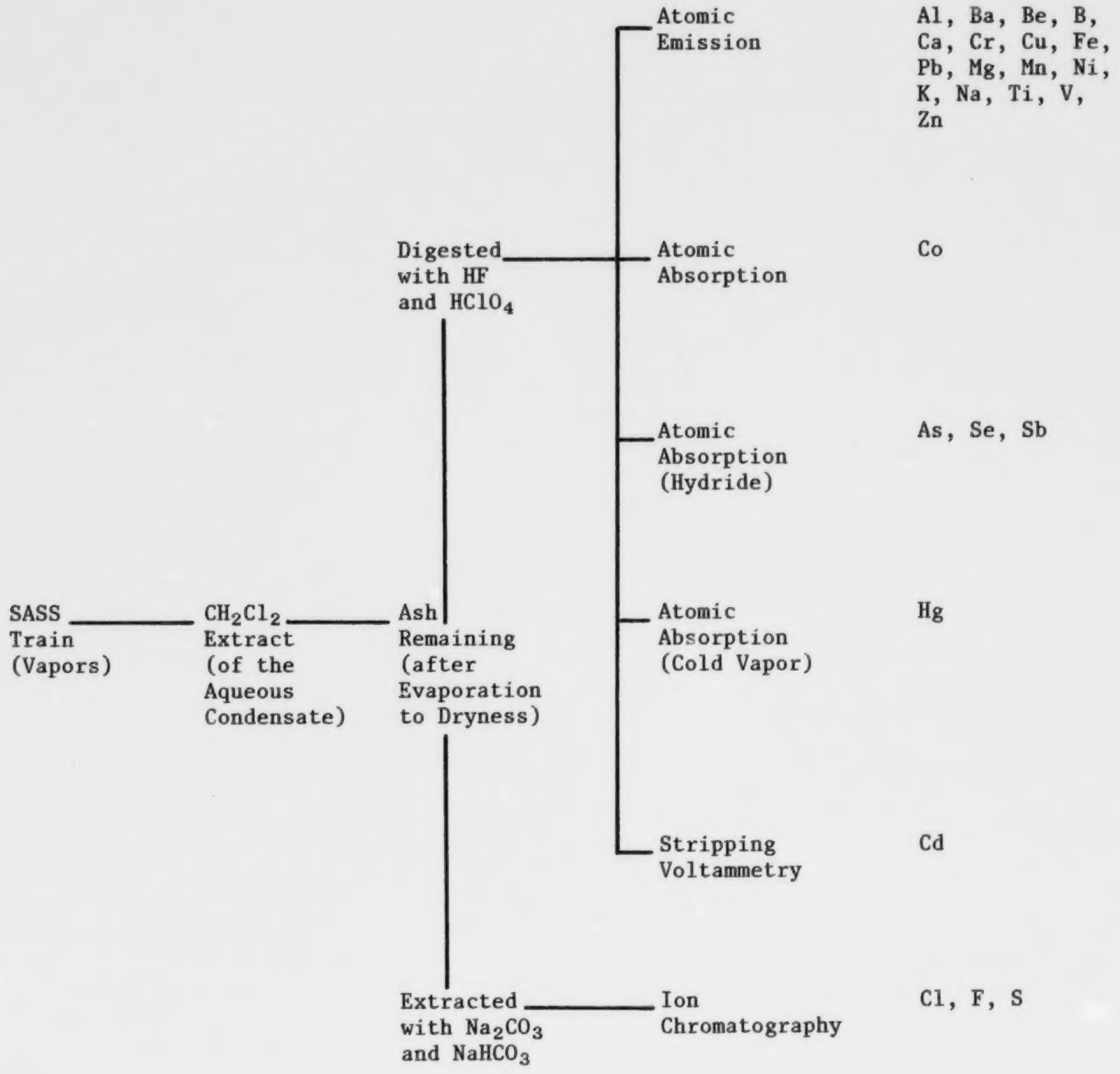
SASS Train (Vapors)
CH_2Cl_2 Extract (of the Aqueous Condensate)
Ash Remaining (after Evaporation to Dryness)
Digested with HF and $HClO_4$
Extracted with Na_2CO_3 and $NaHCO_3$
Atomic Emission
Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn
Atomic Absorption
Co
Atomic Absorption (Hydride)
As, Se, Sb
Atomic Absorption (Cold Vapor)
Hg
Stripping Voltammetry
Cd
Ion Chromatography
Cl, F, S

Figure B-9. (Continued)

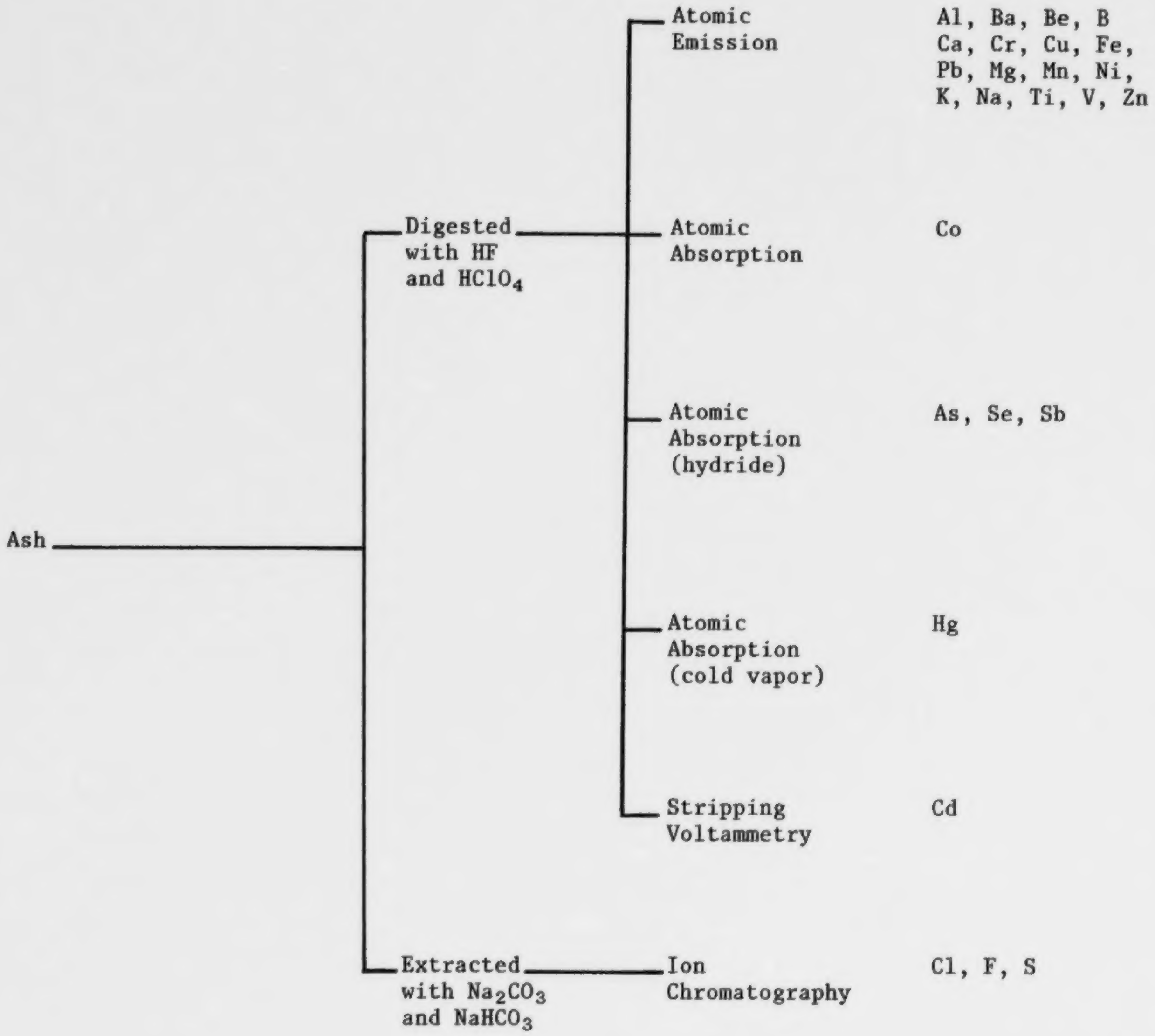
Ash
Digested with HF and HClO4
Extracted with Na2CO3 and NaHCO3
Atomic Emission
Al, Ba, Be, B Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn
Atomic Absorption
Co
Atomic Absorption (hydride)
As, Se, Sb
Atomic Absorption (cold vapor)
Hg
Stripping Voltammetry
Cd
Ion Chromatography
Cl, F, S

Figure B-10. Analytical procedures for trace elements in the Brink impactor fine particulate.

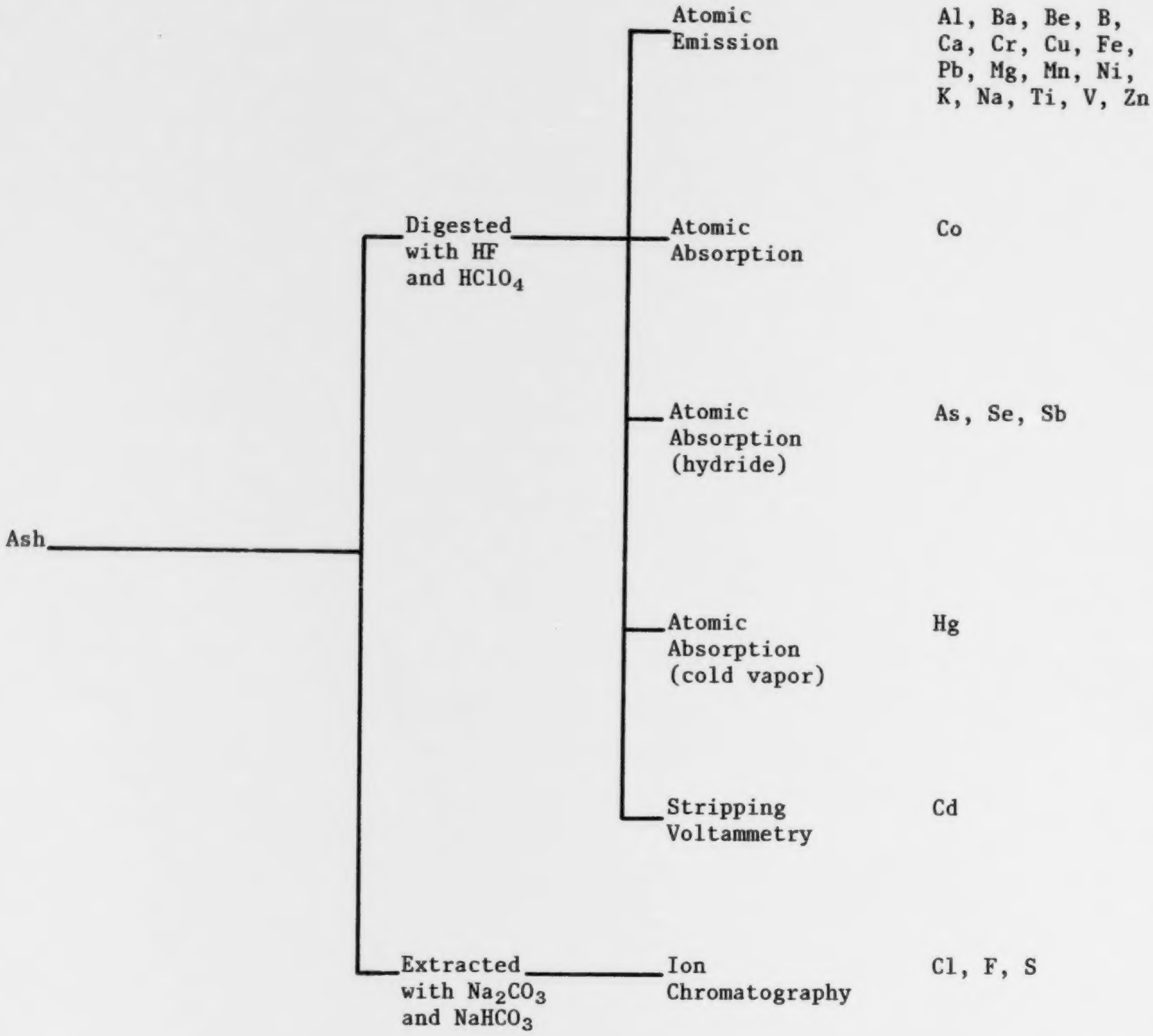
Ash
Digested with HF and $HClO_4$
Extracted with Na_2CO_3 and $NaHCO_3$
Atomic Emission
Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn
Atomic Absorption
Co
Atomic Absorption (hydride)
As, Se, Sb
Atomic Absorption (cold vapor)
Hg
Stripping Voltammetry
Cd
Ion Chromatography
Cl, F, S

Figure B-11. Analytical procedures for trace elements in the Andersen impactor fine particulate.

1.b Ashing of Coal Samples for Hydrofluoric Acid-Aqua Regia Digestion

One gram of the air-dried, pulverized coal sample was accurately weighed in a 40 ml Coors porcelain crucible (Fisher Scientific Co., Fairlawn, NJ). It was ashed according to ASTM Standard D3174 (1) by placing the crucible containing the sample in a cold muffle furnace with the temperature control set at 500°C. During heating, oxidizing conditions were maintained by forcing air at about 1 l/min through the furnace. This assured complete combustion of the coal. Compressed air entered a 1/4-inch stainless tube located in front of the furnace and exited through a 1/4-inch tube in the rear (8). After heating the sample for 1 h, the temperature of the furnace was increased to 750°C and heating continued at this temperature for 3 h thereafter. After cooling to room temperature, the ash was quantitatively transferred with a camel hair brush to a teflon beaker for digestion (2).

Plastic ware was used for the following operations since boron was sought and would be leached by HF from glassware. Twenty ml of freshly prepared Aqua Regia and 20 ml of reagent grade HF were added to the sample in the beaker. The slurry was evaporated just to dryness in a sand bath at a temperature not greater than 220°C. The residue was redissolved by warming for a few minutes with 1 ml of redistilled HNO_3 and 5 ml of deionized water. Another 30 ml of water was added, and the solution was warmed an additional 30 minutes to complete the dissolution. After cooling, 1 ml of redistilled HNO_3 was added, and the solution was diluted to 100 ml in a plastic graduated cylinder.

1.c Cd in Coal Ash by Digestion with Hydrofluoric Acid-Aqua Regia and Determination by Graphite Furnace-Atomic Absorption

An aliquot of the solution prepared in Section 1.b was analyzed for Cd by graphite furnace atomic absorption (3).

1.d Be, B, Cr, Cu, Fe, Pb, Ni, V, and Zn in Coal Ash by Digestion with Hydrofluoric Acid-Aqua Regia and Determination by Atomic Emission

An aliquot of the solution prepared in Section 1.b was analyzed for Be, B, Cr, Cu, Fe, Pb, Ni, V, and Zn by inductively coupled argon plasma atomic emission (ICP) (4). Automatic background correction was required for B, Ni, and Pb. A background factor of 0.55 instead of 1 was used for Pb to make the values determined by ICP agree with those certified for the NBS SRM 1632 coal and 1633 coal ash (5).

1.e Ba, Ca, Mg, Mn, Si, and Ti in Coal by Fusion with Lithium Metaborate and Determination by Atomic Emission

An accurately weighed sample (0.5 g) of air-dried, pulverized coal prepared in Section 1.a was mixed with 2.0 g of reagent grade lithium metaborate in a platinum crucible and heated in a muffle furnace at 900°C until a clear melt was obtained. The mixture was cooled and placed in a beaker containing 8 ml of reagent grade HNO_3 and 150 ml of deionized water. The mixture was stirred vigorously until all material dissolved, and tartaric acid was added at a concentration of 1 percent (2.5 g per 250 ml). The solution was made up to a final volume of 250 ml with deionized water in a volumetric flask (7). An aliquot of this solution was used to determine the concentration of Ba, Ca, Mg, Mn, Si, and Ti by atomic emission (4).

1.f Al, Co, Na, and K in Coal by Fusion with Lithium Metaborate and Determination by Atomic Absorption

An aliquot of solution prepared in Section 1.e was used to determine Al, Co, Na, and K by atomic absorption (6).

1.g As, Se, and Sb in Coal by Ignition with Eschka's Mixture and Determination by Hydride Generation-Atomic Absorption

An accurately weighed sample (1.0 g) of air-dried, pulverized coal prepared in Section 1.a was mixed with 1.5 to 2.0 grams of Eschka's mixture (2 parts by weight of light calcined magnesium oxide to one part of anhydrous sodium carbonate) in a 40 ml Coors porcelain crucible. This mixture was covered with an additional 1.5 grams of Eschka's mixture. The crucible was placed in a cold muffle furnace and heated to 500°C for 1 hour, and then the temperature was increased to 750°C for 3 hours. It was necessary to maintain oxidizing conditions while ashing; therefore, air was forced at one litre/minute through a 1/4-inch stainless steel tubing located in the front of the furnace. Selenium was totally lost from coal in the absence of oxidizing conditions. Exhausted gases passed through a 1/4-inch stainless steel tube in the back of the furnace (8). The crucible was cooled and the contents stirred with a platinum rod. If any unburned coal remained, the crucible was returned to the furnace and heated until all coal was ashed. The ash was transferred to a 150 ml beaker which contained 20 ml hot deionized water and 3 grams of tartaric acid. The crucible was rinsed carefully with 5 ml of concentrated reagent grade HCl and mixed with the contents in the beaker. Two additional 5 ml aliquots of concentrated HCl were added to the mixture and stirred after each addition. If any ash remained, additional acid was added to bring all material into solution. The solution was then diluted to a final volume of 100 ml with deionized water. This solution was used to determine the concentrations of Se, Sb, and As by hydride generation-atomic absorption.

For Se, an aliquot of this solution was mixed with an equal amount of concentrated reagent grade HCl and heated in a boiling steam bath for at least 20 minutes to reduce Se(VI) to Se(IV). The selenium was converted to the hydride by adding $SnCl_2$ (9). The gaseous selenium hydride was swept into an argon-diluted, air-entrained hydrogen flame of an atomic absorption spectrophotometer (6).

For Sb, an aliquot of the final solution was diluted to 50 ml. To reduce the antimony, HCl, KI, and $SnCl_2$ were added to the solution. Sodium borohydride was added to convert antimony to the hydride (10).

The gaseous antimony hydride was swept into an argon-diluted air-entrained hydrogen flame of an atomic absorption spectrophotometer (6,10).

For As, an aliquot of the final solution was diluted to 50 ml. HCl, KI, $SnCl_2$, and powdered zinc were added to generate the arsine for determination by atomic absorption spectrometry (11).

1.h Cl in Coal by Ignition with Eschka's Mixture and Determination by Potentiometric Titration

An accurately weighed sample (1.0 gram) of air-dried, pulverized coal prepared in Section 1.a was mixed with three grams of Eschka mixture in a porcelain crucible. This mixture was covered with an additional two grams of Eschka mixture. The crucible was placed in a cold muffle furnace and gradually heated to 675 ± 25°C within one hour and maintained at this temperature for an hour thereafter. An air flow of 1 l/min was maintained during ignition to assure complete combustion (see Section 1.b). The mixture was stirred with a platinum rod; if any unburned coal remained, the crucible was returned to the furnace and heated until all coal was ashed. The ash was dissolved in 50 percent (V/V) nitric acid and the chloride was determined by potentiometric titration with a standard solution of silver nitrate (12).

1.i F in Coal by Oxygen Bomb Combustion and Determination by Ion Selective Electrode

One gram of air-dried, pulverized coal prepared in Section 1.a was accurately weighed into a combustion crucible, placed in a combustion bomb containing 5 ml of 1 M NaOH, and ignited under oxygen at a pressure of 20-30 atmospheres (2-3 MPa). The pH of the resulting solution was adjusted to 5.0 with 0.5 N H_2SO_4. After addition of 5 ml of citrate buffer solution and dilution to 100 ml, the fluoride was determined potentiometrically by ion selective electrode (13).

1.j Hg in Coal by Oxygen Bomb Combustion and Determination by Cold Vapor Atomic Absorption

About 1 g of air-dried, pulverized coal prepared according to Section 1.a was accurately weighed into a combustion crucible, placed in a combustion bomb containing 10 ml of 10 percent HNO_3, and ignited under oxygen at a pressure of 20-30 atmospheres (2-3 MPa). The mercury trapped in the 10 percent HNO_3 was determined by cold vapor atomic absorption (6,14).

1.k S in Coal by Induction Furnace Combustion

An accurately weighed sample (about 60 mg) of the air-dried, pulverized coal prepared in Section 1.a was covered with iron chip and tin metal accelerators and burned by induction furnace heating in a stream of oxygen (14a). The SO_2 released was passed through an antimony trap to remove interference by halogens (15) and trapped in dilute hydrochloric acid containing potassium iodide and azide. The azide removed interference by nitrogen oxides (15), and the sulfur was determined by titration with standard potassium iodate (14).

2 Analytical Procedures for Trace Elements in Electrostatic Precipitator (ESP) Ash

Figure B-2 gives the analytical procedures for trace elements in electrostatic precipitator ash.

2.a Preparation of ESP Ash Samples

The ash was removed from sealed containers without further preparation for chemical analysis.

2.b Cd in ESP Ash by Digestion with Hydrofloric Acid-Aqua Regia and Determination by Graphite Furnace-Atomic Absorption

About 0.2 g of the ESP ash was accurately weighed in a teflon beaker, digested with HF-Aqua Regia according to Section 1.b, and analyzed according to Section 1.c.

2.c Be, B, Cr, Cu, Fe, Pb, Ni, V, and Zn in ESP Ash by Digestion with Hydrofluoric Acid-Aqua Regia and Determination by Atomic Emission

An aliquot of the solution prepared in Section 2.b was analyzed according to Section 1.d.

2.d Ba, Ca, Mg, Mn, Si, and Ti in ESP Ash by Fusion with Lithium Metaborate and Determination by Atomic Emission

About 0.5 g of the ESP ash was accurately weighed in a platinum crucible. This was digested with lithium metaborate and analyzed as described in Section 1.e.

2.e Al, Co, Na, and K in ESP Ash by Fusion with Lithium Metaborate and Determination by Atomic Absorption

An aliquot of the solution prepared in Section 2.d was analyzed according to Section 1.f.

2.f As, Se, and Sb in ESP Ash by Ignition with Eschka's Mixture and Determination by Hydride Generation-Atomic Absorption

About 0.6 g of the ESP ash was accurately weighed in a 40 ml Coors porcelain crucible. This was digested with Eschka's mixture and analyzed as described in Section 1.g.

2.g F in ESP Ash by Oxygen Bomb Combustion and Determination by Ion Selective Electrode

About 0.2 g of ESP ash was accurately weighed in a combustion crucible containing exactly 1 g of air-dried, pulverized coal previously assayed for fluorine according to Section 1.i. After the sample was thoroughly mixed, it was assayed for fluorine according to the oxygen bomb combustion-ion selective electrode method described in Section 1.i. The difference between the results for the mixture of ESP ash and coal and the coal alone gave the concentration of fluorine in the ESP ash (16).

2.h Hg in ESP Ash by Digestion with Aqua Regia and Determination by Cold Vapor Atomic Absorption

About 0.2 g of ESP ash was accurately weighed in a glass bottle. Deionized water and aqua regia were added, and the solution was heated in a water bath at 95°C. The solution was cooled, diluted with deionized water, treated with $KMnO_4$, and heated in a water bath. Sodium chloride-hydroxylamine sulfate was added to reduce excess permanganate. Stannous sulfate was added to form atomic mercury for determination by cold vapor atomic absorption (6).

2.i S in ESP Ash by Induction Furnace Combustion

An accurately weighed sample of ESP ash (about 60 mg) was analyzed as described in Section 1.k.

2.j Cl in ESP Ash by Extraction and Determination by Ion Chromatography

About 50 mg of the ESP Ash was accurately weighed in a 50 ml pyrex beaker. Five ml of a solution 0.0024 M in Na_2CO_3 and 0.003 M in $NaHCO_3$ was pipetted into the beaker. The beaker was sealed with aluminum foil and sonified with heating for an hour to extract the chloride. The supernatant was decanted, centrifuged, and an aliquot was assayed for Cl by ion chromatography (17).

3 Analytical Procedures for Trace Elements in the Impinger Water from the Total Particulate Train

Figure B-3 gives the analytical procedures for trace elements in the impinger water from the total particulate train.

3.a Al, Ba, Be, Ca, Cu, Fe, Mg, Mn, Ti, V, Zn, B, Si, and Na in Impinger Water by Atomic Emission

An aliquot of the impinger water sample was used for the direct determination by inductively coupled argon plasma atomic emission (4).

3.b K in Impinger Water by Atomic Absorption

An aliquot was aspirated for determination (6).

3.c Cd, Pb, Cr, Co, and Ni in Impinger Water by Solvent Extraction and Determination by Atomic Absorption

These elements were determined by chelation and extraction with methylisobutylketone and analyzed by atomic absorption (6).

3.d Se in Impinger Water by Digestion with Permanganate and Determination by Hydride Generation-Atomic Absorption

Selenium was determined after digestion by hydride generation-atomic absorption (6,9).

3.e As and Sb in Impinger Water by Digestion with H_2SO_4 and HNO_3 and Determination by Hydride Generation-Atomic Absorption

As and Sb were determined by evaporating a 100 ml aliquot with 7 ml of (1+1) H_2SO_4 and 5 ml of concentrated HNO_3 to SO_3 fumes. After cooling, 25 ml of deionized water was added, and the fuming repeated to expel nitrogen oxides. An aliquot was removed for analysis by hydride generation-atomic absorption (10,11).

3.f Cl in Impinger Water by Digestion with Acidic Peroxide and Determination by Potentiometric Titration with $AgNO_3$

Chloride was determined by potentiometric titration after digestion with peroxide to destroy the sulfite (18).

3.g S in Impinger Water by Digestion with Peroxide and Determination by Turbidimetry

The pH of an aliquot of the impinger water was adjusted, if necessary, to 2 with (1+4) HCl. One-half ml of 30 percent H_2O_2 was added to exactly 5 ml of the impinger water, and the solution allowed to digest for 1 h at room temperature. This provided time for the peroxide to oxidize all the sulfite to sulfate (19-21). The sulfur was measured by turbidimetry (18).

3.h F in Impinger Water by Ion Selective Electrode

F was determined by ion selective electrode after adjusting the pH to 5.0-5.5 (6).

4 Analytical Procedures for Trace Elements in the Ash From the Total Particulate Train (TP Ash)

Figure B-4 gives the analytical procedures for trace elements in the ash from the total particulate train.

4.a Preparation of the TP Ash Samples

Three kinds of ash samples were collected by the total particulate train: (1) the free, dry fine particulate ash sample trapped by the cyclone, hereinafter called the dry catch sample; (2) the particulate impinged on glass fiber filters, hereinafter called the filter sample; and (3) the residue formed after evaporating the organic solvent used to remove particulate from the probe, hereinafter called the probe rinse sample. In order to determine 26 elements by microchemical analysis, two aliquots are needed--one for Cl, F, S; another for Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn.

Dry Catch Samples

The dry catch samples for test numbers 114-112 with weights of 0.5 to 1.7 g were dried under an infrared lamp for about 10 min. The samples were broken up with a platinum rod, pulverized with a rubber policeman, transferred to a plastic cup, and desiccated over silica gel for at least 30 min. before weighing two aliquots for microchemical analysis.

Filter Samples

The particulate on the filter samples for test numbers 114-122 with field-determined weights of 1.4 to 3.0 g was dislodged with a platinum rod, transferred to a plastic cup, ground to a fine powder with a rubber policeman, mixed, and desiccated over silica gel for at least 30 min. before weighing two aliquots for microchemical analysis.

Since the particulate on filter samples for test numbers 214-322 with field-determined weights of 0.01 to 0.5 g was too small or too tightly embedded to dislodge for microchemical analysis, it was washed off with absolute ethanol. This served to isolate the particulate from the background concentrations of trace elements in the unexposed filter (22). Specifically, the field identification number that was handwritten in ink on the back of the filter was removed by cutting it out with stainless steel scissors to eliminate a possible trace element blank for the ink. The diameter of the filter was measured to determine whether it was 63.5, 90, or 102 mm, so that the respective blanks could be prepared. When chloride, fluoride, and sulfur analysis was requested in addition to the other 23 elements (Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn), it was necessary to divide the sample. The whole filter was placed on a teflon board. Then a teflon wedge, one-fourth the size of the filter, was used as a guide to remove a quarter of the filter by cutting with a surgical steel scapel. The one-quarter section of the filter was saved for the Cl, F, and S determination; and the three-quarter section was saved for determination of 23 elements (Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn). Si was not determined because of the large sample requirement (0.5 g) and the high background concentration of silica in the glass fiber filter substrate.

The whole, three-quarter, or one-quarter section of each filter was dried on aluminum foil under an infrared lamp for 10 minutes, followed by air-drying to constant weight in the room atmosphere while loosely covered with foil. Prior desiccation over silica gel caused poor reproducibility during weighing in the room atmosphere. The tare weight was measured to the nearest one-hundredth of a milligram. The filter for 23 elements was removed from the foil with platinum-tipped forceps and placed in the 100 ml Teflon beaker; absolute ethanol was added to cover the filter, and particulate was removed by placing the beaker briefly in an ultrasonic bath. A 50 ML pyrex beaker was used to extract one-quarter filters for Cl, F, and S. The extracted filter was removed from the beaker with platinum-tipped forceps, dried, and reweighed to determine the weight of ash transferred. The ethanol in the beaker was evaporated without boiling, dried, and desiccated over silica gel in a desiccator until chemical analysis was initiated. The glass fiber filters shed a little during the extraction, so this additional weight diluted the sample. The blank weights for the unexposed filters extracted concurrently with the samples are given in Tables B-II and B-III.

Probe Rinse Samples

The particulate in the probe rinse samples, received in 250 ml pyrex beakers for test numbers 114-122 with weights of 3.0-5.0 g, was dried under an infrared lamp for about 10 min, broken up with a platinum rod, pulverized with a rubber policeman, transferred to a plastic cup, and desiccated over silica gel for at least 30 min before weighing two aliquots for microchemical analysis.

The particulate in the probe rinse samples, received in 250 ml pyrex beakers for test numbers 214-222 and 314 with weights of 0.1-0.5 g, was dried under an infrared lamp for about 10 min, dislodged from the walls of the beaker, crushed with a rubber policeman, and desiccated over silica gel for at least 30 min before weighing two aliquots for microchemical analysis. Field data for the probe rinse with test number 221 showed a weight of 0.028 g. Since there appeared to be more sample, its total weight was determined by adding the weights withdrawn for chemical analysis (that removed for Cl, F, and S plus that removed for Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, Co, As, Se, Sb, Hg, and Cd) to that remaining (determined by washing with absolute ethanol, drying, and reweighing). The new weight of the probe rinse with test number 221 was 0.22719 g, which is considerably greater than that of 0.028 g reported in the field.

TABLE B-II

WEIGHTS OF TOTAL PARTICULATE ASH USED FOR DETERMINATION OF 23 ELEMENTS[a]

Test number	Filter, weight used, g	Dry catch, weight used, g	Probe rinse, weight used, g
114	0.50347	0.50192	0.50037
115	0.50069	0.50258	0.50066
116	0.49912	0.50223	0.49964
117	0.50113	0.49931	0.49958
119	0.50180	0.50301	0.49968
120	0.50054	0.49987	0.50004
121	0.50005	0.49963	0.50113
122	0.49966	0.09964	0.50223
214	0.09782(1)[b]		0.10056
215	0.07300(1)[b]		0.10146
216	0.04213(1)[b]		0.10163
217	0.09166(1)[b]		0.09924
219	0.15011(1)[b]		0.10315
220	0.23696(1)[b]		0.10071
221	0.05358(1)[b]		0.10050
222	0.11023(1)[b]		0.10191
314	0.02061(2)[b]		0.08124
315	0.02043(3)[b]		0.03208
316	0.01908(3)[b]		0.02196
317	0.01811(3)[b]		0.03053
319	0.01700(4)[b]		0.02287
321	0.01159(5)[b]		0.10820
322			
Filter Blank	0.00246[c]		
Filter Blank	0.00423[c]		
Filter Blank	0.00167[c]		
Filter Blank	0.00291[c]		
Filter Blank	0.00184[c]		

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[a] Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn.

[b] Filter blank numbers 1-5 go with designated samples: (1) three-fourths of a 102 mm microquartz filter; (2) a whole 90 mm spectrograde glass fiber filter; (3) three-fourths of a 90 mm spectrograde glass fiber filter; (4) a whole 63.5 mm spectrograde Andersen glass fiber filter; (5) three-fourths of a 63.5 mm spectrograde Andersen glass fiber filter.

[c] This is weight determined by extracting the designated unexposed filter with absolute ethanol.

TABLE B-III

WEIGHTS OF TOTAL PARTICULATE ASH USED FOR DETERMINATION OF 3 ELEMENTS[a]

Test number	Filter weight used, g	Dry catch weight used, g	Probe rinse weight used, g
114	0.10212	0.10234	0.10079
115	0.09890	0.10590	0.10131
116	0.10179	0.10360	0.10106
117	0.10017	0.09865	0.10317
119	0.09920	0.10062	0.09917
120	0.10123	0.10110	0.10257
121	0.09992	0.10126	0.09923
122	0.09867	0.10272	0.10207
214	0.04076(1)[b]		0.10300
215	0.02942(1)[b]		0.09938
216	0.02816(1)[b]		0.10122
217	0.03296(1)[b]		0.09892
219	0.06938(1)[b]		0.10010
220	0.10869(1)[b]		0.10134
221	0.02278(1)[b]		0.09771
222	0.08460(1)[b]		0.09730
314			
315	0.01024(2)[b]		0.01010
316	0.01774(2)[b]		0.01473
317	0.00768(2)[b]		0.00464
319			
321	0.00760(3)[b]		0.01445
322	0.00674(4)		0.03051
Filter Blank 1	0.00103[c]		
Filter Blank 2	0.00072[c]		
Filter Blank 3	0.00083[c]		
Filter Blank 4	0.00022[c]		

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[a] Cl, F, and S

[b] Filter blank numbers 1-4 go with designated samples: (1) one-fourth of a 102 mm microquartz filter; (2) one-fourth of a 90 mm spectrograde glass fiber filter; (3) one-fourth of a 63.5 mm spectrograde Andersen glass fiber filter; (4) a whole 63.5 mm spectrograde Andersen glass fiber filter.

[c] This weight was determined by extracting the designated unexposed filter with absolute ethanol.

The particulate in the probe rinse samples, received in 250 ml pyrex beakers for test numbers 315-317 and 321 with weights of 0.03 to 0.05 g, was dried under an infrared lamp for about 10 min and mixed with a platinum rod; the small amount adhering to the platinum rod was quantitatively transferred to a tarred 50 ml pyrex beaker. Absolute ethanol was added to the beaker. The platinum rod with adhering particulate was dipped in the ethanol and sonified to assure that the particulate was completely removed. After evaporation, desiccation, and reweighing to determine the weight of the sample, the residue in 50 ml pyrex beaker was saved for the determination of Cl, F, and S. The dry sample remaining in the 250 ml pyrex beaker was extracted by sonification with absolute ethanol, quantitatively transferred to a tarred 50 ml teflon beaker, evaporated, desiccated, reweighed, and saved for determination of 23 elements (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, Co, As, Se, Sb, Hg, and Cd).

The probe rinse for test number 319 with weight of 0.02 g was not divided because only one aliquot of sample was needed to determine the aforementioned 23 elements that were requested. Also, the probe rinse for test number 322 with weight of 0.01 g was not divided because only one portion was needed for the determination of the three elements, Cl, F, and S, that were requested.

The division of the probe rinse samples into two aliquots for microchemical analysis of (1) Cl, F, S, and (2) Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn was made on the solid residue left after extraction of the probe in the field. The latter procedure may have altered the elemental distribution (e.g., sulfur compounds may extract during probe cleanup, making the residue heterogeneous). Use of the whole sample for 3 or 23 elements is probably a better choice than dividing it into two aliquots, which may be different from each other, for determining 3 elements in 1 aliquot and 23 elements in the other.

4.b Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, and Zn in TP Ash by Digestion with Hydrofluoric Acid-Perchloric Acid and Determination by Atomic Emission

Table B-II shows the weights of the total particulate ash (TP ash) samples used for digestion with hydrofluoric acid-perchloric acid for determination of Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, As, Se, Sb, Hg, Cd, and Co after preparation according to Section 4.a.

TP ash samples in Table B-II with weights of about 0.5 g were digested in 50 ml or 100 ml teflon beakers with 5 ml of HF (Ultrex grade, Baker Chemical Co., Phillipsburg, N.J.) and one drop (0.05 ml) of $HClO_4$ (Double Distilled from Vycor Grade, G. Frederick Smith Co., Columbus, Ohio) (23).

Plastic or teflon ware was used exclusively to prepare and dispense reagents to guard against contamination from boron, a common ingredient in glassware. The mixture was evaporated slowly, without boiling, just to dryness in a sand bath at a temperature not exceeding 220°C. The residue was not baked to guard against losses by volalitization. The evaporation was repeated a second time with 3 ml of HF and one drop of $HClO_4$ and a third time with 2 ml of HF and one drop of $HClO_4$. After cooling, the salts formed by this triple evaporation were moistened with 1.25 ml of hydrochloric acid (Ultrex grade, Baker Chemical Co., Phillipsburg, N.J.). After having allowed a few minutes for dissolution, the mixture was diluted with 12.5 ml of deionized water, covered with a watch glass, and heated just below boiling for about five minutes or longer, as necessary, to dissolve the salts and large clumps of particulate. When the solution had cooled, the watch glass and beaker were washed with 2 ml of 5 percent (V/V) hydrochloric acid (Ultrex grade, Baker Chemical Co., Phillipsburg, N.J.), and the solution was poured through a plastic funnel into a 25 ml volumetric flask. After rinsing the beaker with an additional 20 drops (1 ml) of 5 percent (V/V) hydrochloric acid and combining this with the solution in the volumetric flask, the solution was diluted to exactly 25 ml with 5 percent (V/V) hydrochloric acid. Immediately the solution was poured into a 30 ml polyethylene bottle, capped, and saved for the determination of 23 elements.

TP ash samples in Table B-II with weights of about 0.1 g or less were digested in 50 ml teflon beakers with 1.5 ml of HF and one drop (0.05 ml) of perchloric acid. The HF and HCl were Ultrex grade that were obtained from Baker Chemical Co., Phillipsburg, N.J. The $HClO_4$ was the Double Distilled from Vycor Grade from G. Frederick Smith Co., Columbus, Ohio. The mixture was evaporated slowly, without boiling, just to dryness in a sand bath at a temperature not exceeding 220°C. The evaporation was repeated a second time with 1 ml of HF and 1 drop of $HClO_4$ and a third time with 1 ml of HF and 1 drop of $HClO_4$. After cooling, the salts formed by this triple evaporation were moistened with 0.50 ml of HCl. After having allowed a few minutes for dissolution, the mixture was diluted with 5.0 ml of deionized water, covered with a watch glass, and heated just below boiling for about 5 minutes or longer, as necessary, to dissolve the salts and large clumps of particulate. When the solution had cooled, the watch glass and beaker were washed with 20 drops (1 ml) of 5 percent (V/V) HCl, and the solution was poured through a plastic funnel into a 10 ml volumetric flask. After rinsing the beaker with an additional 20 drops (1 ml) of 5 percent (V/V) hydrochloric acid and combining this with the solution in the volumetric flask, the solution was diluted to exactly 10 ml with 5 percent (V/V) hydrochloric acid. Immediately, the solution was poured into a 20 ml polyethylene bottle, capped, and saved for the determination of 23 elements.

An aliquot of this solution was analyzed for Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, and Zn by inductively coupled argon plasma atomic emission (ICP) (4). Automatic background correction was required for Ni, B, and Pb. A correction factor of 0.55 instead of 1 was used for Pb to make the value determined by ICP agree with that certified for the NBS SRM 1633 coal ash (5). The value for Ba was multiplied by 27/16 to make it agree with the NBS SRM 1633 coal ash (5) value found by neutron activation in an interlaboratory study (24). Except for the very small samples (<0.05 g), determinations for Al, Ca, Fe, Mg, Mn, and Ti were made portions of the digestate that had been diluted 21-fold with 5 percent (V/V) HCl (Ultrex grade, Baker Chemical Co., Phillipsburg, N.J.). The other elements were determined by ICP without dilution.

4.c Co in TP Ash by Digestion with Hydrofluoric Acid-Perchloric Acid and Determination by Atomic Absorption

An aliquot of solution prepared in Section 4.b was used to determine Co by atomic absorption (6).

4.d As, Se, and Sb in TP Ash by Digestion with Hydrofluoric Acid-Perchloric Acid and Determination by Hydride Generation-Atomic Absorption

Arsenic was determined by diluting exactly 1 ml of solution prepared in Section 4.b to 50 ml with deionized water. HCl, KI, $SnCl_2$, and powdered zinc were added to generate the arsine for determination by atomic absorption spectrometry (11).

Antimony was determined by diluting exactly 1 ml of solution prepared in Section 4.b to 50 ml with deionized water. HCl, KI, and $SnCl_2$ were added to reduce the antimony. Sodium borohydride was added to convert antimony to the hydride (10). The hydride was swept into an argon-diluted air-entrained hydrogen flame of an atomic absorption spectrometer (6,10).

Selenium was determined by adding exactly 1 ml of the solution prepared in Section 4.b to a mixture of 5 ml of concentrated HCl and 10 ml of 25 percent (W/V) ammonium chloride and was heated in a boiling steam bath for at least 20 minutes to reduce selenium(VI) to selenium(IV). The selenium was converted to the hydride by adding $SnCl_2$ (9), and the hydride was swept into an argon-diluted air-entrained hydrogen flame of an atomic absorption spectrometer (6).

4.e Hg in TP Ash by Digestion with Hydrofluoric Acid-Perchloric Acid and Determination by Cold Vapor Atomic Absorption

A 1 ml of the solution prepared in Section 4.b was used to determine mercury by micro-cold vapor atomic absorption (25).

4.f Cd in TP Ash by Digestion with Hydrofluoric Acid-Perchloric Acid and Determination by Anodic Stripping Voltammetry

A 1 ml of the solution prepared in Section 4.b was treated with 2.0 ml of redistilled HNO_3. After evaporation to dryness and redissolution in ammonium citrate, the concentration of Cd was determined by differential pulse anodic stripping voltammetry (26).

4.g Cl, F, and S in TP Ash by Extraction with Na_2CO_3-$NaHCO_3$ and Determination by Ion Chromatography

Table III shows the weights of the total particulate ash (TP ash) samples used for extraction with Na_2CO_3-$NaHCO_3$ for determination of Cl, F, and S by ion chromatography after preparation according to Section 4.a.

The value for F is for the free, soluble portion only because the fluorosilicates are probably not extracted.

TP ash samples in Table B-III with weights of about 0.1 g were accurately weighed in a 50 pyrex beaker. Four ml of a solution 0.0024 M in Na_2CO_3 and 0.003 M in $NaHCO_3$ were pipetted into the beaker. After sealing the beaker with aluminum foil and sonifying with heating for a half an hour, the supernatant was decanted, centrifuged, and an aliquot was assayed for Cl, F, and S by ion chromatography (17). The concentration of sample was 2.5 percent as compared to 1 percent for Cl only in Section 2.j to increase the reading for fluoride so it could be quantified more accurately.

TP ash samples with weights less than 0.05 g, which were prepared in 50 ml pyrex beakers as described in Section 4.a, were treated with 2 ml instead of 4 ml of the 0.0024 M Na_2CO_3-0.003 M $NaHCO_3$.

Except for the dry catch for test number 122, TP ash samples for test numbers 114-117 and 119-122 were also analyzed for S by induction furnace combustion (see Section 2.i) and for F by oxygen bomb combustion-ion selective electrode (see Section 2.g).

5 Analytical Procedures for Trace Elements in the Gases From the Vapor Phase Train

Figure B-5 gives the analytical procedures for trace elements in the gases from the vapor phase train. The reagents used for the collection of gaseous trace elements were K_2CO_3, KOH, and H_2O_2. The K_2CO_3 reagent matrix was 2%(w/v) K_2CO_3 in water; the KOH reagent matrix was 0.25 M KOH in water; the H_2O_2 reagent matrix was a mixture of 3%(v/v) (1.8 M) H_2O_2, 0.14 M HNO_3, and 0.02 M $AgNO_3$ in water. All reagents except K_2CO_3 were reagent grade. The K_2CO_3 was Ultrex grade from Baker Chemical Co., Phillipsburg, N.J. The K_2CO_3 and KOH samples were analyzed by the same procedures.

5.a Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Na, Pb, Ti, V, Zn, Si, and B in the K_2CO_3 or KOH Impinger Solution with Acidification and Determination by Atomic Emission

A 1.0 ml aliquot of the K_2CO_3 or KOH sample was placed in a 10 ml test tube and acidified with 50 µl redistilled HNO_3. The sample was diluted with 1.0 ml of deionized water. After mixing, the final solution was used to determine the concentration of Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Na, Pb, Ti, V, Zn, Si, and B by inductively coupled argon plasma atomic emission spectrometry (4).

5.b Co in the K_2CO_3 or KOH Impinger Solution with Acidification and Determination by Atomic Absorption

An aliquot of the K_2CO_3 or KOH sample was acidified with redistilled nitric acid to a pH <2 and analyzed by atomic absorption (6).

5.c Cl in the K_2CO_3 or KOH Impinger Solution with Digestion in Acidic Peroxide and Determination by Potentiometric Titration with Silver Nitrate

A 25 ml aliquot of the K_2CO_3 or KOH sample was acidified with H_2SO_4 and digested with peroxide; the Cl was determined by potentiometric titration with standard silver nitrate (18).

5.d S in the K_2CO_3 or KOH Impinger Solution with Digestion in Acidic Peroxide and Determination by Turbidimetry

The S was determined as described in Section 3.g.

5.e As and Sb in the K_2CO_3 or KOH Impinger Solution with Acidification and Determination by Hydride-Generation Atomic Absorption

An aliquot of the K_2CO_3 or KOH was neutralized with redistilled nitric acid (G. Frederick Smith Co., Columbus, Ohio). The resulting solution was digested and analyzed for As and Sb by hydride generation-atomic absorption as described in Section 3.e (10,11). Digestion destroys the sulfite, eliminating background from SO_2 released in the acidic media, while sparging prior to injection of the hydride-forming reagent (10,11).

5.f Se in the K_2CO_3 or KOH Impinger Solution with Digestion in Acidic Permanganate and Determination by Hydride-Generation Atomic Absorption

Thirty ml of K_2CO_3 or KOH was acidified with HNO_3 to a pH <2. The sample was treated with 5%(w/v) $KMNO_4$ to maintain a purple tint for at least 30 minutes. This destroys sulfite which causes low results in the next step by reducing selenium salts to the atomic state. An equal volume of concentrated reagent grade HCl was added, and the sample was digested in a steam bath at 95°C for at least 20 minutes. The sample was cooled and diluted with 6M HCl to a known volume and analyzed for selenium by atomic absorption using the gaseous hydride technique (6,9).

5.g F in the K_2CO_3 or KOH Impinger Solution with Adjustment in pH to 5.5 and Determination by Ion Selective Electrode

After adjusting the pH to 5.0-5.5, the F was determined by ion selective electrode (6).

5.h Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V Zn, Si, B, K, and Na in the Peroxide-Silver Nitrate Impinger Solution by Atomic Emission

An aliquot of the peroxide-silver nitrate impinger solution was used for the direct determination by inductively coupled argon plasma atomic emission (4).

5.i Co in the Peroxide-Silver Nitrate Impinger Solution by Atomic Absorption

These samples were determined by direct atomic absorption (6).

5.j Cl in the Peroxide-Silver Nitrate Impinger Solution by Gravimetry

A 10.0 ml aliquot of the peroxide-silver nitrate impinger solution was diluted to 100 ml with deionized water and filtered through a preweighed glass fiber filter. The filter was rinsed with deionized water, dried at 110°C, and reweighed. The difference in weight was the chlorine capture (27).

5.k F in the Peroxide-Silver Nitrate Impinger Solution with Adjustment in pH and Determination by Ion Selective Electrode

An aliquot of this solution was mixed with an equal volume of buffer (pH 5.0-5.5) in a plastic beaker. The concentration of fluoride was determined potentiometrically by ion selective fluoride electrode (6).

5.1 Se in the Peroxide-Silver Nitrate Impinger Solution by Digestion with Acidic Permanganate and Determination by Hydride Generation-Atomic Absorption

A 30.0 ml aliquot of this solution was treated with a sufficient amount of reagent grade 5%(w/v) $KMnO_4$ (about 7 ml) to maintain a purple tint for at least 30 minutes. The permanganate destroys the peroxide (28). An equal volume of concentrated reagent grade HCl was added, and the sample was digested in a steam bath at 95°C for at least 20 minutes. The solution was cooled and diluted with 6M HCL to 100 ml. The concentration of selenium was determined by atomic absorption using the gaseous hydride technique (6,9).

5.m As and Sb in the Peroxide-Silver Nitrate Impinger Solution by Digestion with Nitric Acid-Sulfuric Acid and Determination by Hydride Generation Atomic Absorption

A 20.0 ml aliquot of this solution was digested to SO_3 fumes with 5.0 ml of concentrated redistilled HNO_3 and 5.0 ml reagent grade (1+1) H_2SO_4. After cooling, 10 ml of distilled water and 10 ml of concentrated redistilled HNO_3 were added. The solution was fumed again, and the concentration of arsenic and antimony was determined by atomic absorption using the gaseous hydride technique (10,11).

5.n S in the Peroxide-Silver Nitrate Impinger Solution by Turbidimetry

Silver in the peroxide-silver nitrate impinger solution interfered with the turbidimetric determination (18) of sulfate since a sulfate spike of the clear solution produced a precipitate. Therefore, the silver was removed from the solution by precipitation with a slight excess of 0.020 M NaCl and, after settling, by filtering the supernatant through a glass fiber filter and determining sulfate in the filtrate by turbidimetry (18). The solubility of Ag_2SO_4 and of Ag_2SO_3, too, limits the usefulness of a mixture of peroxide and silver nitrate for collecting sulfur dioxide.

6 Analytical Procedures for Mercury Collected by the Mercury Vapor Phase Train

The reagents used for the collection of mercury vapor were K_2CO_3 and $KMnO_4$ in HNO_3. There were three types of samples from the mercury train (K_2CO_3 , $KMnO_4$ in HNO_3), and an oxalic acid rinse of the impingers that contained the $KMnO_4$ solution. The K_2CO_3 was 10%(w/v) K_2CO_3 in water; the $KMnO_4$ in HNO_3 was 3%(w/v) $KMnO_4$ in 14.2%(v/v) HNO_3; the oxalic acid used for rinsing was 10%(w/v) oxalic acid. All reagents except K_2CO_3 were reagent grade. The K_2CO_3 was Ultrex grade from Baker Chemical Co., Phillipsburg, N.J.

6.a Hg in the K_2CO_3 Impinger Solution by Cold Vapor Atomic Absorption

The mercury concentration was determined by acidifying 100 ml of sample with 5.0 ml of concentrated reagent grade H_2SO_4. Thereafter, the solution was treated for mercury by the cold vapor atomic absorption technique beginning with Section 8.1 on page 124 in the cited reference (6).

6.b Hg in the $KMnO_4$ in HNO_3 Impinger Solution by Cold Vapor Atomic Absorption

A 10.0 ml sample of the $KMnO_4$ matrix was diluted to 100.0 ml with deionized water. Thereafter, the solution was treated for mercury by the cold vapor atomic absorption technique beginning with Section 8.1 on page 124 in the cited reference (6). Hydroxylamine was added until the permanganate color just dissipated.

6.c Hg in the Oxalic Acid Rinse by Cold Vapor Atomic Absorption

A 75.0 ml sample of the oxalic acid rinse was diluted to 100.0 ml with deionized water. Five milliliters of concentrated reagent grade H_2SO_4 and 2.5 ml of concentrated redistilled HNO_3 were added. Hydroxylamine and stannous chloride were added to generate atomic mercury for determination by the cold vapor atomic absorption technique (6). Calibration was achieved in oxalic acid having the same concentration as that employed for the diluted sample. Permanganate was not used to digest the sample because permanganate is consumed endlessly by the oxalic acid.

7 Analytical Procedures for Trace Elements in the Ash from the SASS Train (SASS Ash)

Figure B-7 shows the analytical procedures for trace elements in ash from the SASS train. This test for particulates captured by the SASS train was made by Monsanto Research Corp.

7.a Preparation of the SASS Ash Samples

Four kinds of ash samples were collected by the SASS train: (1) the particulate impinged on glass fiber filters, hereinafter called the filter sample; (2) the residue formed after evaporating the organic solvent used to remove particulate from the filter housing, hereinafter called the filter housing rinse sample; (3) the free, dry fine particulate sample trapped by the cyclone, hereinafter called the cyclone catch sample; (4) the residue formed after evaporating the organic solvent used to remove particulate from the cyclone, hereinafter called the cyclone rinse sample. The SASS train contained three cyclones that produced three dry catch and cyclone rinse samples with pore sizes of about 1 μ, 3 μ, and 10 μ.

Since the weight of the particulate caught by the cyclones and filter in the SASS train was not determined by Monsanto in the field, it was measured by TVA's Environmental Laboratory in Chattanooga. These weights are displayed in Table B-IV. The procedure for this task is explained in the following narrative.

Total Weight of Filter and Filter Housing Rinse Samples

The filter samples were air-dried to constant weight in the room atmosphere while loosely covered with aluminum foil. After weighing, the tare weight provided by Monsanto Research Corp. (27) was subtracted to determine the total weight of the samples. See Table B-IV for results.

The filter housing rinse samples were received in (1 + 1) CH_2Cl_2-CH_3OH. This mixture for each sample was evaporated to dryness in a tarred Teflon beaker under an infrared lamp and, after desiccation over silica gel for at least 30 min, was reweighed to determine the weight added. See Table B-IV for weights.

Total Weight of Cyclone Rinse and Catch Samples

Cyclone rinse samples were received in (1 + 1) CH_2Cl_2-CH_3OH. This mixture for each sample of given pore size was evaporated to dryness in a tarred Teflon beaker under an infrared lamp and, after desiccation over silica gel for at least 30 min, was reweighed to determine the weight added. See Table B-IV for weights.

The cyclone catch samples with test numbers KMS-229, KMS-231, and KMS-233 that were received in polyethylene bottles were washed with absolute ethanol into tarred Teflon beakers containing the corresponding

TABLE B-IV

TOTAL WEIGHTS OF SASS PARTICULATE SAMPLES

Test number	Type of sample	Weight sample, g
KMS-228	10 μ Cyclone Rinse	0.03536
KMS-229	10 μ Cyclone Rinse	0
KMS-230	3 μ Cyclone Rinse	0.01853
KMS-231	3 μ Cyclone Catch	0
KMS-232	1 μ Cyclone Rinse	0.00521
KMS-233	1 μ Cyclone Catch	0
KMS-234	17-19 Filter	0.14149
KMS-235	Filter Housing Rinse	0.00655
KMS-243	10 μ Cyclone Rinse	0.29867
KMS-244	10 μ Cyclone Catch	59.00936
KMS-245	3 μ Cyclone Rinse	0.45637
KMS-246	3 μ Cyclone Catch	57.30177
KMS-247	1 μ Cyclone Rinse	0.16067
KMS-248	1 μ Cyclone Catch	20.48918
KMS-249	10-16 Filter	0.25364
	10-18 Filter	0.24786
	17-22 Filter	0.20620
	17-23 Filter	0.24395
	17-24 Filter	0.33095
KMS-251	Filter Housing Rinse	0.01331
KMS-259	1+3+10 μ Cyclone Rinse and Catch	16.30666

cyclone rinse samples having the same pore size. After evaporation to dryness under an infrared lamp, and desiccation over silica gel for at least 30 min, the beaker was reweighed to determine weight added. Table IV shows that the weight of the cyclone catch was nil.

The cyclone catch samples with test numbers KMS-244, KMS-246, and KMS-248 were weighed directly by pouring the fine particulate powder into tarred plastic cups. These weights are given in Table IV.

Preparation of Filter and Filter Housing Samples for Chemical Analysis

Since the particulate in filter samples for test numbers KMS-234 and KMS-249 was too small or too tightly embedded to dislodge for microchemical analysis, it was washed off with absolute ethanol. This served to isolate the particulate from the background concentrations of trace elements in the unexposed filter (22). Since Cl, F, and S analyses were requested in addition to the other 23 elements (Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn), it was necessary to divide the sample. The filter was placed on a teflon board. Then a teflon wedge, one-fourth the size of the filter, was used as a guide to remove a quarter of the filter by cutting with a surgical steel scapel. The one-quarter section of the filter was saved for the Cl, F, and S determination; and the three-quarter section was saved for determination of 23 elements (Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn). Si was not determined because of the large sample requirement (0.5 g) and the high background concentration of silica in the glass fiber filter substrate.

The three-quarter or one-quarter section of each filter was dried on aluminum foil under an infrared lamp for 10 minutes, followed by air-drying to constant weight in the room atmosphere while loosely covered with foil. Prior desiccation over silica gel caused poor reproducibility during weighing in the room atmosphere. The tare weight was measured to the nearest one-hundredth of a milligram. The three-quarter filter for the 23 elements was removed from the foil with platinum-tipped forceps, and placed in the 100 ml Teflon beaker; absolute ethanol was added to cover the filter, and particulate was removed by placing the beaker briefly in an ultrasonic bath. A 50 ml pyrex beaker was used to extract one-quarter filters for Cl, F, and S. The extracted filter was removed from the beaker with platinum-tipped forceps, dried, and reweighed to determined the weight of ash transferred. Compositing of 5 filters was requested for KMS-249, so the process was repeated for the three-quarter or one-quarter section of each filter, and the sum of the individual ash weights transferred yielded the total composited weight of sample.

Also, compositing of the filter housing rinse with that from the filter was requested. Therefore, about one-fourth of the residue in the Teflon beaker from the determination of total weight of filter housing rinse was transferred with a platinum rod to the 50 ml pyrex beaker containing the ethanol and particulate rinsed from the one-quarter filters. Any particulate adhering to the platinum rod was dipped in the ethanol and sonified to assure that the particulate had been quantitatively transferred. After evaporation, desiccation, reweighing the Teflon beaker to determine the weight of sample removed and adding that weight to that rinsed from the one-quarter filters, the solution in the 50 ml pyrex beaker was evaporated to dryness, desiccated over silica gel, and saved for determination of Cl, F, and S. After having removed about one-fourth of the filter housing rinse sample in the Teflon beaker for Cl, F, and S, the rest of the sample in the Teflon beaker was washed with absolute ethanol into a Teflon beaker containing the ethanol and particulate from the three-quarter filters. After evaporation, desiccation, and reweighing the Teflon beaker that once contained the filter housing rinse to determine the weight of sample transferred and adding that weight to that rinsed from the three-quarter filters, the solution in the teflon beaker was evaporated to dryness, desiccated over silica gel, and saved for determination of 23 elements (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, Co, As, Se, Sb, Hg, and Cd).

The glass fiber filters shed a little during the extraction, so this additional weight diluted the sample. The blank weights for the unexposed filters extracted concurrently with the samples are given in Tables B-V and B-VI.

Preparation of Cyclone Rinse and Catch Samples for Chemical Analysis

The cyclone catch samples for test numbers KMS-244, KMS-246, KMS-248, and KMS-259 were saved without further preparation for weighing two aliquots for microchemical analysis. Although requested, the cyclone rinse samples with test numbers KMS-243, KMS-245, and KMS-247 were not composited with the cyclone catch samples having test numbers of KMS-244, KMS-246, and KMS-248, respectively, because of the great difference in total sample weights shown in Table B-IV. Instead, cyclone rinse samples with test numbers of KMS-243, KMS-245, and KMS-247 were analyzed separately. However, the results for elemental concentrations in the cyclone rinse can be combined mathematically, if desired, with those for the cyclone catch to yield a composited result. The particulate for these samples in the Teflon beakers from the total weight determinations was dislodged from the walls of the Teflon beakers with a rubber policeman, desiccated over silica gel, and saved for weighing two aliquots for microchemical analysis.

The particulates in the composited cyclone rinse and catch samples in the Teflon beakers from the total weight determinations given in Table B-IV for KMS-228 plus KMS-229, KMS-230 plus KMS-231, and KMS-232 plus KMS-233 were each split into two samples. The particulate in the Teflon beakers for these composited samples with known tare weights was dried under an infrared lamp for about 10 min and mixed with a platinum rod; the small amount adhering to the platinum rod quantitatively was transferred to a 50 ml pyrex beaker. The Teflon beaker was reweighed to determine the weight of sample added. Absolute ethanol was added to the pyrex beaker. The platinum rod with adhering particulate was dipped in the ethanol and sonified to assure that the particulate was completely removed. After evaporation, the residue in 50 ml pyrex beaker was desiccated and saved for the determination of Cl, F, and S. The dry sample remaining in the Teflon beaker was then calculated by subtracting the tare weight of the empty beaker. This sample was saved for determination of 23 elements (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, Co, As, Se, Sb, Hg, and Cd).

As mentioned in the foregoing narrative, the division of the cyclone rinse plus catch samples into two aliquots for microchemical analysis of (1) Cl, F, S, and (2) Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn was made on the solid residue left after treating with an organic in the field and then absolute ethanol in the laboratory. The latter procedure may have altered the elemental distribution, e.g., sulfur compounds may extract during cyclone cleanup in the field or during compositing with ethanol in the laboratory, making the residue heterogeneous. Use of the whole sample for chemical analysis for 3 or 23 elements is probably a better choice than dividing it into two aliquots, which may be different from each other, for determining 3 elements in 1 aliquot and 23 elements in the other.

7.b Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na,Ti, V, and Zn in SASS Ash by Digestion with HF-$HClO_4$ and Determination by Atomic Emission

Table B-V shows the weights of SASS ash samples used for digestion with hydrofluoric acid-perchloric acid for determination of Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, As, Se, Sb, Hg, Cd, and Co after preparation according to Section 4.a.

SASS ash samples in Table B-V with weights of about 0.5 g were digested by the procedure in Section 4.b for the 0.5 g TP ash samples. SASS ash samples in Table B-V with weights of about 0.2 g or less were digested by the procedure in Section 4.b for the 0.1 g or less TP ash samples.

An aliquot of the digested solution was analyzed by ICP as described in Section 4.b.

7.c Co in SASS Ash by Digestion with HF-$HClO_4$ and Determination by Atomic Absorption

An aliquot of solution prepared in Section 7.b was used to determine Co by atomic absorption (6).

7.d As, Se, and Sb in SASS Ash by Digestion with HF-$HClO_4$ and Determination by Hydride Generation-Atomic Absorption

The solution prepared in Section 7.b was used to determine As, Se, and Sb as described in Section 4.d.

TABLE B-V

WEIGHTS OF SASS ASH USED FOR DETERMINATION OF 23 ELEMENTS[a]

Composite of Test Numbers	Type of Sample	Weight Sample, g
KMS-228 +KMS-229	10 μ cyclone rinse and catch	0.03184
KMS-230 +KMS-231	3 μ cyclone rinse and catch	0.01460
KMS-232 +KMS-233	1 μ cyclone rinse and catch	0.00381
KMS-234 +KMS-235	17-19 filter[b] + filter housing rinse	0.03948
KMS-243	10μ cyclone rinse	0.09922
KMS-244	10μ cyclone catch	0.49947
KMS-245	3μ cyclone rinse and catch	0.10332
KMS-246	3μ cyclone catch	0.49652
KMS-247	1μ cyclone rinse and catch	0.10075
KMS-248	1μ cyclone catch	0.50321
KMS-249 +KMS-251	10-16 + 10-18 + 17-22 + 17-23 + 17-24 filters[b] + filter housing rinse	0.21430
KMS-259	1+3+10μ cyclone rinse and catch	0.49888
Filter blank	SASS filter[b]	0.00666[c]

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[a] Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn.

[b] Three-fourths of an unexposed SASS filter was used for the blank.

[c] This is weight determined by extracting three-fourths of an unexposed SASS filter with absolute ethanol.

7.e Hg in SASS Ash by Digestion with HF-$HClO_4$ and Determination by Cold Vapor Atomic Absorption

1 ml of the solution prepared in Section 7.b was used to determine mercury by micro-cold vapor atomic absorption (25).

7.f Cd in SASS Ash by Digestion with HF-$HClO_4$ and Determination by Stripping Voltammetry

1 ml of the solution prepared in Section 7.b was treated with 2.0 ml of redistilled HNO_3. After evaporation to dryness and redissolution in ammonium citrate, the concentration of Cd was determined by differential pulse anodic stripping voltammetry (26).

7.g Cl, F, and S in SASS Ash by Extraction with Na_2CO_3-$NaHCO_3$ and Determination by Ion Chromatography

Table B-VI gives the weights of SASS ash samples used for extraction with Na_2CO_3-$NaHCO_3$ for determination of Cl, F, and S by ion chromatography after preparation according to Section 7.a.

SASS ash samples in Table B-VI with weights of about 0.1 g were extracted and analyzed by the procedure in Section 4.g for the 0.1 g TP ash samples. SASS ash samples with weights less than 0.05 g were also extracted and analyzed by the procedure in Section 4.g for the less than 0.05 g TP ash samples.

SASS ash samples for test numbers KMS244-246, 248, and 259 were also analyzed for S by induction furnace combustion (see Section 2.2) and for F by oxygen bomb combustion-ion selective electrode (see Section 2.g).

8 Analytical Procedures for Trace Elements in the XAD-2 Resin from the SASS Train

Figure B-8 displays the analytical procedures for trace elements in the XAD-2 resin from the SASS train. The SASS train was operated by Monsanto Research Corp.

8.a Preparation of the XAD-2 Resin Samples

The XAD-2 resin samples were removed from sealed containers without further preparation for chemical analysis. There was sufficient sample, 110-120 g, for ordinary chemical analysis.

8.b Ashing of XAD-2 Resin Samples for Digestion with HF-$HClO_4$

One gram of the XAD-2 resin was accurately weighed in a 40 ml Coors porcelain crucible (Fisher Scientific Co., Fairlawn, N.J.) and ashed as

TABLE VI

WEIGHTS OF SASS ASH USED FOR DETERMINATION OF 3 ELEMENTS[a]

Composite of test numbers	Type of Sample	Weight sample, g
KMS-228 +KMS-229	10μ cyclone rinse and catch	0.00519
KMS-230 +KMS-231	3μ cyclone rinse and catch	0.00252
KMS-232 +KMS-233	1μ cyclone rinse and catch	0.00029
KMS-234 +KMS-235	17-19 filter[b] + filter housing rinse	0.01962
KMS-243	10μ cyclone rinse	0.10150
KMS-244	10μ cyclone catch	0.09995
KMS-245	3μ cyclone rinse and catch	0.09882
KMS-246	3μ cyclone catch	0.09982
KMS-247	1μ cyclone rinse and catch	0.03765
KMS-248	1μ cyclone catch	0.09970
KMS-249 +KMS-251	10-16 + 10-18 + 17-22 + 17-23 + 17-24 filters[b] + filter housing rinse	0.04421
KMS-259	1+3+10μ cyclone rinse and catch	0.10194
Filter blank	SASS filter[b]	0.00326[c]

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[a] Cl, F, and S.

[b] One-fourth of an unexposed SASS filter was used for the blank.

[c] This is weight determined by extracting one-fourth of an unexposed SASS filter with absolute ethanol.

described in Section 1.b. After cooling to room temperature, the small amount of ash remaining (none was visible for the blank, but black specs were visible for the sample) was transferred quantitatively to a teflon beaker by washing and sonifying with absolute ethanol. This slurry was evaporated to dryness under an infrared lamp, desiccated over silica gel, and saved for digestion with $HF\text{-}HClO_4$.

8.c Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, and Zn in the XAD-2 Resin Ash by Digestion with $HF\text{-}HClO_4$ and Determination by Atomic Emission

The residue from the XAD-2 resin remaining in the Teflon beaker after preparation by Section 8.b was digested with $HF\text{-}HClO_4$ using the procedure for the 0.1 g samples of TP ash given in Section 4.g and analyzed for Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, and Zn by ICP as described in Section 4.b.

8.d Co in XAD-2 Resin Ash by Digestion with $HF\text{-}HClO_4$ and Determination by Atomic Absorption

An aliquot of solution prepared in Section 8.c was used to determine Co by atomic absorption (6).

8.e Cd in XAD-2 Resin Ash by Digestion with $HF\text{-}HClO_4$ and Determination by Anodic Stripping Voltammetry

A 1 ml of the solution prepared in Section 8.c was treated with 2.0 ml of redistilled HNO_3. After evaporation to dryness and redissolution in ammonium citrate, the concentration of Cd was determined by differential pulse anodic stripping voltammetry (26).

8.f As, Se, and Sb in the XAD-2 Resin by Ignition with Eschka's Mixture and Determination by Hydride Generation-Atomic Absorption

See Section 1.g to learn procedure used to determine As, Se, and Sb in the XAD-2 resin.

8.g Hg in the XAD-2 Resin by Digestion with Aqua Regia and Determination by Cold Vapor Atomic Absorption

See Section 2.h for procedure.

8.h S in the XAD-2 Resin by Induction Furnace Combustion

See Section 1.k for procedure for total sulfur. Also, 0.1 g of the XAD-2 resin was accurately weighed in a 50 ml pyrex beaker and analyzed for S by ion chromatography as described in Section 4.g. This is an extractable S value.

8.i F in the XAD-2 Resin by Extraction with Na_2CO_3-$NaHCO_3$ and Determination by Ion Chromatography

About 0.1 g of the XAD-2 resin was accurately weighed in a 50 ml pyrex beaker and treated for F and Cl as described in Section 4.g for the 0.1 g TP ash samples. This value for F is for the free, soluble portion only because the fluorosilicates are probably not extracted. The XAD-2 resin was not treated for F by the oxygen bomb combustion-ion selective electrode method employed for coal in Section 1.i because of the possible explosion hazard. The value for Cl is an extractable value only.

8.j Cl in the XAD-2 Resin by Ignition with Eschka's Mixture and Determination by Potentiometric Titration

This sample was analyzed for total Cl as described in Section 1.h.

9 Analytical Procedures for Trace Elements in the Gases from the SASS Train

Figure B-9 shows the analytical procedures for trace elements in the gases from the SASS train. The reagents used to collect the gaseous trace elements were H_2O_2 and persulfate with silver nitrate. The H_2O_2 was 6M H_2O_2 in water, and the persulfate with silver nitrate was a mixture of 0.2 M $(NH_4)_2S_2O_8$, 0.28 M HNO_3, and 0.04 M $AgNO_3$ in water. Reagent grade chemicals were used to prepare solutions (Fisher Scientific Co., Fairlawn, N.J.).

Also, there was a persulfate with silver nitrate impinger solution into which had been added an unknown volume of 50% (V/V) isopropyl alcohol, an aqueous condensate catch sample which had been extracted with methylene chloride, and the methylene chloride extract of the aqueous condensate.

The only sample from the SASS train not analyzed was the 50% (V/V) isopropyl alcohol rinse of the empty impingers.

9.a Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, and Na in the Peroxide Impinger Solution by Atomic Emission

An aliquot of the peroxide impinger solution was used for the direct determination by inductively coupled argon plasma atomic emission (4).

9.b Co in the Peroxide Impinger Solution by Atomic Absorption

These samples were determined by direct atomic absorption (6).

9.c Cl in the Peroxide Impinger Solution by Digestion with H_2SO_4 and Potentiometric Titration with $AgNO_3$

H_2SO_4 was added, the solution digested, and the Cl determined by potentiometric titration with standard silver nitrate (18).

9.d F in the Peroxide Impinger Solution by Adjustment in pH to 5.5 and Determination by Ion Selective Electrode

After adjusting the pH to 5.0-5.5, the F was determined by ion selective electrode (6).

9.e Se in the Peroxide Impinger Solution by Digestion with Acidic Permanganate and Determination by Hydride Generation-Atomic Absorption

See Section 5.e to learn procedure.

9.f As and Sb in the Peroxide Impinger Solution by Digestion with HNO_3 and H_2SO_4 and Determination by Hydride Generation-Atomic Absorption

See Section 5.m for procedure employed.

9.g S in the Peroxide Impinger Solution by Turbidimetry

Sulfur was determined by turbidimetry (18) after verifying the solution was acidic (pH ~ 1-4).

9.h Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, and Na in the Persulfate with $AgNO_3$ Impinger Solution by Atomic Emission

An aliquot of this solution was used for direct determination by inductively coupled argon plasma atomic emission (4).

9.i Co in the Persulfate with $AgNO_3$ Impinger Solution by Atomic Absorption

These samples were determined by direct atomic absorption (6).

9.j Cl in the Persulfate with $AgNO_3$ Impinger Solution by Gravimetry

See Section 5.j to learn procedure used.

9.k F in the Persulfate with $AgNO_3$ Impinger Solution by Adjustment in pH to 5.5 and Determination by Ion Selective Electrode

Refer to Section 5.k for method.

9.l Se in the Persulfate with $AgNO_3$ Impinger Solution by Digestion with Acidic Permanganate and Determination by Hydride Generation-Atomic Absorption

See Section 5.l to learn method.

9.m As and Sb in the Persulfate with $AgNO_3$ Impinger Solution by Digestion with HNO_3 and H_2SO_4 and Determination by Hydride Generation-Atomic Absorption

See Section 5.m for procedure.

9.n S in the Persulfate with $AgNO_3$ Impinger Solution by Turbidimetry

See Section 5.n to learn procedure.

9.o Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, and Na in the Persulfate with $AgNO_3$ Impinger Solution Containing the Isopropyl Alcohol Rinse by Evaporation to Dryness, Dissolution in HNO_3, and Determination by Atomic Emission

The persulfate with $AgNO_3$ impinger solution was diluted in the field with an unknown amount of a 50% (v/v) isopropyl alcohol rinse that would probably alter the viscosity of the solution sufficiently to interfere by changing the uptake rate when determining elements by ICP (4). Because of this interference, it would be better to collect the isopropyl rinse separately.

Therefore, the isopropyl alcohol was removed by evaporating a 50 ml aliquot of this solution carefully in a teflon beaker just to dryness on a heated sand bath at a temperature below 220°C. This procedure was not entirely effective in removing the isopropyl alcohol, as a gelatinous mass formed indicating a reaction had taken place between the isopropyl alcohol and the oxidizing ingredients in the solution. Ethanol would have been a better rinsing agent than isopropyl alcohol because it is less reactive chemically.

The gelatinous residue was redissolved by warming a few minutes with a mixture of 1 ml of redistilled HNO_3 and 5 ml of deionized water. Then the solution was diluted to 50 ml. An aliquot of this solution was used for direct determination by inductively coupled argon plasma atomic emission (4). Since a spike of the elements sought was recovered from this solution, the gelatinous residue did not sufficiently alter the viscosity of the solution to interfere.

9.p Co in the Persulfate with $AgNO_3$ Impinger Solution Containing the Isopropyl Alcohol Rinse by Evaporation to Dryness, Dissolution in HNO_3, and Determination by Atomic Absorption

The samples prepared in Section 9.o were determined by direct atomic absorption (6).

9.q Cl in the Persulfate with $AgNO_3$ Impinger Solution Containing the Isopropyl Alcohol Rinse by Gravimetry

An aliquot of this solution was assayed by the procedure in Section 5.j.

9.r F in the Persulfate with $AgNO_3$ Impinger Solution Containing the Isopropyl Alcohol Rinse by Adjustment in pH to 5.5 and Determination by Ion Selective Electrode

See Section 5.k to learn method.

9.s Se in the Persulfate with $AgNO_3$ Impinger Solution Containing the Isopropyl Alcohol Rinse by Digestion with Acidic Permanganate and Determination by Hydride Generation- Atomic Absorption

See Section 5.l to learn method.

9.t As and Sb in the Persulfate with $AgNO_3$ Impinger Solution Containing the Isopropyl Alcohol Rinse by Digestion with HNO_3 and H_2SO_4 and Determination by Hydride Generation-Atomic Absorption

Refer to Section 5.m for procedure.

9.u S in the Persulfate with $AgNO_3$ Impinger Solution Containing the Isopropyl Alcohol Rinse by Turbidimetry

See Section 5.n to learn procedure.

9.v Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn, Si, B, K, and Na in the Aqueous Condensate by Atomic Emission

An aliquot of this sample was used for the direct determination by inductively coupled argon plasma atomic emission (4).

9.w Co in the Aqueous Condensate by Atomic Absorption

An aliquot was aspirated for determination (6).

9.x Cl in the Aqueous Condensate by Digestion with Peroxide and Potentiometric Titration with $AgNO_3$.

See Section 3.f. for procedure.

9.y F in the Aqueous Condensate by Adjustment in pH and Determination by Ion Selective Electrode

See Section 3.h. for procedure.

9.z Se in the Aqueous Condensate by Digestion with Acidic Permanganate and Determination by Hydride Generation-Atomic Absorption

See Section 3.d to learn procedure.

9.aa As and Sb in the Aqueous Condensate by Digestion with HNO_3 and H_2SO_4 and Determination by Hydride Generation-Atomic Absorption

Refer to Section 3.e for procedure.

9.ab S in the Aqueous Condensate by Turbidimetry

The sulfur was measured directly by turbidimetry (18). Digestion with peroxide that was used in Section 3.g to oxidize any sulfite to sulfate (19-21) probably would have improved accuracy.

9.ac Preparation of the Methylene Chloride Extract of the Aqueous Condensate (MCE)

The methylene chloride extract was evaporated to dryness in a tarred Teflon beaker under an infrared lamp. After desiccation over silica gel and reweighing to determine the total weight of sample, the sample was divided into two aliquots as follows.

The particulate in the Teflon beaker with known tare weight was mixed with a platinum rod, and the small amount adhering to the platinum rod was quantitatively transferred to a 50 ml pyrex beaker. The Teflon beaker was reweighed to determine the weight of the sample added. Absolute ethanol was added to the pyrex beaker. The platinum rod with adhering particulate was dipped in the ethanol and sonified to assure that the particulate was completely removed. After evaporation, the residue in 50 ml pyrex beaker was desiccated and saved for the determination of Cl, F, and S. The dry sample remaining in the Teflon beaker was then calculated by subtracting the tare weight of the empty beaker. This sample was saved for determination of 23 elements (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, Co, As, Se, Sb, Hg, and Cd).

Table B-VII gives the volume of methylene chloride extracts received, the total weight of the samples, and weights used for chemical analysis. The pure methylene chloride itself contributes a little, and this additional weight dilutes the sample. The blank weight for a methylene chloride extract evaporated concurrently with the samples is also given in Table B-VII.

TABLE B-VII

METHYLENE CHLORIDE TOTAL CATCH AND ANALYSIS WEIGHTS

Test Number	Volume, ml	Total Catch, g	Analysis Weight[a], g	Analysis Weight[b], g
KMS-236	698	0.33198	0.25167	0.07096
KMS-252	900	0.09819	0.03464	0.02900
KB-227[c]	900	-	0.00233	-
KB-227[c]	600	-	0.00200	-

[a] Determination of 23 elements (Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn).

[b] Determination of three elements (Cl, F, and S).

[c] This is the pure methylene chloride blank received with the samples.

9.ad Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, and Zn in Ash from the MCE by Digestion with HF-$HClO_4$ and Determination by Atomic Emission

Table B-VII shows the weights of ash samples from the methylene chloride extraction (MCE) used for digestion with hydrofluoric acid-perchloric acid for determination of Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, As, Se, Sb, Hg, Cd, and Co after preparation according to Section 9.ac.

MCE samples in Table B-VII with weights of about 0.25 g or less were digested by the procedure in Section 4.b. for the 0.1 g TP ash samples.

An aliquot of the digested solution was analyzed by ICP as described in Section 4.b.

9.ae Co in Ash from the MCE by Digestion with HF-$HClO_4$ and Determination by Atomic Absorption

An aliquot of solution prepared in Section 9.ad was used to determine Co by atomic absorption (6).

9.af As, Se, and Sb in Ash from the MCE by Digestion with HF-$HClO_4$ and Determination by Hydride Generation-Atomic Absorption

The solution prepared in Section 9.ad was used to determine As, Se, and Sb as described in Section 4.d.

9.ag Hg in Ash from the MCE by Digestion with HF-$HClO_4$ and Determination by Cold Vapor Atomic Absorption

One ml of the solution prepared in Section 9.ad was used to determine mercury by micro-cold vapor atomic absorption (25).

9.ah Cd in Ash From the MCE by Digestion with HF-$HClO_4$ and Determination by Anodic Stripping Voltammetry

One ml of the solution prepared in Section 9.ad was treated with 2.0 ml of redistilled HNO_3. After evaporation to dryness and redissolution in ammonium citrate, the concentration of Cd was determined by differential pulse anodic stripping voltammetry (26).

9.ai Cl, F, and S in Ash from the MCE by Extraction with Na_2CO_3-$NaHCO_3$ and Determination by Ion Chromatography

Table B-VII gives the weights of MCE ash samples used for extraction with Na_2CO_3-$NaHCO_3$ for determination of Cl, F, and S by ion chromatography after preparation according to Section 9.ac. MCE ash samples with weights less than about 0.07 g were extracted and analyzed by the procedure in Section 4.g for the less than 0.05 g TP ash samples.

10 Analytical Procedures for Trace Elements in the Brink Impactor Fine Particulate (Brink Ash)

Figure B-10 shows the analytical procedures for trace elements in the Brink impactor fine particulate (Brink ash).

10.a Preparation of the Brink Ash

The Brink ash samples were received on aluminum pans that were wrapped in aluminum foil and packaged in plastic vials with snap cap lids. In order to obtain sufficient sample weight for analysis, it was necessary to composite samples by tests and plates. Table B-VIII represents the compositing scheme for the Brink ash samples. Cyclone samples (O_c) were received for the following test samples only: 214B2, 219B1, 220B1, and 220B3.

Each sample to be composited according to Table B-VIII was unwrapped, and the aluminum foil and aluminum pan containing the fine particulate was dried for 10 minutes under an infrared lamp and desiccated for 30 minutes over silica gel. The tare weight was measured to the nearest one-hundredth of a milligram. The aluminum pan was placed in a 100 ml Teflon beaker with platinum-tipped forceps and any particulate matter remaining on the aluminum foil was removed with absolute ethanol and poured into the beakers. Additional ethanol was added to the beaker to cover the aluminum pan. The particulate matter was removed from the aluminum pan by placing the beaker briefly in an ultrasonic bath. The pan was removed from the beaker with platinum-tipped forceps and returned to the aluminum foil and dried under an infrared lamp for 10 minutes. After desiccation over silica gel for 30 minutes, the foil and pan were reweighed. The weight extracted was determined by difference.

The next sample to be composited was extracted, dried, and weighed as previously described. This sample was combined with the material in the beaker from the previous sample, and the added weight was determined by the difference between empty and full sample vessels. This process was repeated for each sample to yield the composited samples listed in Table B-VIII. After compositing the samples, the ethanol was evaporated to dryness under an infrared lamp, and the Teflon beaker was stored over silica gel in a desiccator for analysis of 23 elements (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K. Na, Ti, V, Zn, Co, As, Se, Sb, Hg, Cd). The extraction and compositing scheme is similar to that used by Accu-Labs (22).

10.b Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, and Zn in the Brink Ash by Digestion with $HF-HClO_4$ and Determination by Atomic Emission

The composited Brink ash samples prepared in Section 10.a and listed in Table B-VIII were digested with $HF-HClO_4$ by the procedure for the 0.1 g or less samples described in Section 4.b and analyzed by atomic emission as described in that section.

TABLE B-VIII

COMPOSITING SCHEME FOR BRINK IMPACTOR FINE PARTICULATE FOR DETERMINING 23 ELEMENTS[a]

Composite of Field Tests	Composite of Plates	Approximate Particle Size, μ	Extracted Weight, mg
119-B-2+ 115B1+119B1 +121B1+121B2 +121B3	0_c+1	>3	5.69
(See Above)	2+3	1-3	19.30
(See Above)	4+5	0-1	3.04
214B2+ 215B1+219B1 +220B1+ 220B2+220B3	0_c+1	>3	5.25
(See Above)	2+3	1-3	18.45
(See Above)	4+5	0-1	7.50
Aluminum pan	-	-	0.45 0.35
Filter Blank	-	-	-

---

[a] Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, Co, As, Se, Sb, Hg, and Cd.

10.c Co in the Brink Ash by Digestion with HF-$HClO_4$ and Determination by Atomic Absorption

An aliquot of solution prepared in Section 10.b was used to determine Co by atomic absorption (6).

10.d As, Se, and Sb in the Brink Ash by Digestion with HF-$HClO_4$ and Determination by Hydride Generation-Atomic Absorption

The solution prepared in Section 10.b was used to determine As, Se, and Sb as described in Section 4.d.

10.e Hg in the Brink Ash by Digestion with HF-$HClO_4$ and Determination by Cold Vapor Atomic Absorption

One ml of the solution prepared in Section 10.b was used to determine mercury by micro-cold vapor atomic absorption (25).

10.f Cd in the Brink Ash by Digestion with HF-$HClO_4$ and Determination by Anodic Stripping Voltammetry

One ml of the solution prepared in Section 10.b was treated with 2.0 ml of redistilled HNO_3. After evaporation to dryness and redissolution in ammonium citrate, the concentration of Cd was determined by differential pulse anodic stripping voltammetry (26).

11 Analytical Procedures for Trace Elements in the Andersen Impactor Fine Particulate (Andersen Ash)

Figure B-11 gives the analytical procedures for trace elements in the Andersen impactor fine particulate.

11.a Preparation of the Andersen Ash

The Andersen ash samples were received on perforated spectrograde glass fiber stage filters having a diameter of 63.5 mm. These filters were wrapped in aluminum foil for storage. In order to obtain sufficient sample size for analysis, it was necessary to composite samples by tests and plates. Table B-IX gives the compositing scheme for the Andersen ash samples used to determine 23 elements (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, Co, As, Se, Sb, Hg, and Cd). Table B-X gives the scheme for samples used to determine three elements (Cl, F, and S). No cyclone (O_c) samples were received.

Since the particulate on Andersen stage filter samples was too small or too tightly embedded to dislodge by tapping with a platinum rod, it was washed off with absolute ethanol. This served to isolate the particulate from the background concentrations of trace elements in the unexposed filter (22). Specifically, the field identification number that was handwritten in ink on the back of the aluminum foil in which the filters were wrapped was removed with absolute ethanol to eliminate a possible trace element blank for the ink. When chloride, fluoride, and sulfur analyses were requested in addition to the other 23 elements (Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn), it was necessary to divide the sample. The whole filter was placed on a teflon board. Then a teflon wedge, one-fourth the size of the filter, was used as a guide to remove a quarter of the filter by cutting with a surgical steel scalpel. The one-quarter section of the filter was saved for the Cl, F, and S determination, and the three-quarter section was saved for determination of 23 elements (Al, Sb, As, Ba, Be, B, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Na, Ti, V, and Zn). Si was not determined because of the large sample requirement (0.5 g) and the high background concentration of silica in the glass fiber filter substrate.

The whole, three-quarter, or one-quarter section of each filter was dried on aluminum foil under an infrared lamp for 10 minutes, followed by drying to constant weight over silica gel in a desiccator. The tare weight was measured to the nearest one-hundredth of a milligram. The filter for 23 elements was removed from the foil with platinum-tipped forceps, and placed in the 100 ml Teflon beaker; absolute ethanol was added to cover the filter, and particulate was removed by placing the beaker briefly in an ultrasonic bath. A 50 ml pyrex beaker was used to extract one-quarter filters for Cl, F, and S. The extracted filter was removed from the beaker with platinum-tipped forceps, dried, and reweighed to determine the weight of ash transferred. The next sample to be composited was extracted, dried, and weighed as previously described. This sample was combined with the material in the beaker from the previous sample, and the added weight was determined by the difference between empty and full sample vessels. This process was repeated for each sample to yield the composited samples listed in Tables B-IX and B-X. After compositing the samples, the ethanol was evaporated to dryness under an infrared lamp and the beaker was stored in a desiccator for analysis of 23 elements (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, Co, As, Se, Sb, Hg, Cd) or for analysis of three elements (F, Cl, and S).

The glass fiber filters shed a little during the extraction, so this additional weight diluted the sample. The blank weights for the unexposed filters extracted concurrently with the samples are given in Tables B-IX and B-X.

11.b Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, and Zn in the Andersen Ash by Digestion with $HF-HClO_4$ and Determination by Atomic Emission

The composited Andersen ash samples prepared in Section 11.a and listed in Table B-IX were digested with $HF-HClO_4$ by the procedure for the 0.1 g or less samples described in Section 4.b and analyzed by atomic emission as described in that section.

TABLE B-IX

COMPOSITING SCHEME FOR ANDERSEN IMPACTOR FINE PARTICULATE FOR DETERMINING 23 ELEMENTS[a]

Composite of Field Tests	Composite of Plates	Approximate Particle Size, μ	Extracted Weight, mg
219A1+219A2	0_c+1+2+3[b]	>3	63.00
(See Above)	4+5[c]	1-3	39.67
(See Above)	6+7+8[b]	0-1	65.83
214A+215A +220A1+220A2 +221A1+221A2	0_c+1+2+3[c]	>3	85.31
(See Above)	4+5[c]	1-3	54.09
(See Above)	6+7+8[c]	0-1	48.42
322A	0_c+1+2+3[b]	>3	19.87
(See Above)	4+5[b]	1-3	11.35
(See Above)	6+7+8[b]	0-1	11.89
Filter Blank	-	-	3.05[c] 4.37[b]

---

[a] Al, Ba, Be, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Ti, V, Zn, Co, As, Se, Sb, Hg, and Cd.

[b] Three-fourths of an Andersen stage filter was used.

[c] A whole Andersen stage filter was used.

11.c Co in the Andersen Ash by Digestion with $HF-HClO_4$ and Determination by Atomic Absorption

An aliquot of solution prepared in Section 11.b was used to determine Co by atomic absorption (6).

11.d As, Se, and Sb in the Andersen Ash by Digestion with $HF-HClO_4$ and Determination by Hydride Generation-Atomic Absorption

The solution prepared in Section 11.b was used to determine As, Se, and Sb as described in Section 4.d.

11.e Hg in the Andersen Ash by Digestion with $HF-HClO_4$ and Determination by Cold Vapor Atomic Absorption

One ml of the solution prepared in Section 11.b was used to determine mercury by micro-cold vapor atomic absorption (25).

11.f Cd in the Andersen Ash by Digestion with $HF-HClO_4$ and Determination by Anodic Stripping Voltammetry

One ml of the solution prepared in Section 11.b was treated with 2.0 ml of redistilled HNO_3. After evaporation to dryness and redissolution in ammonium citrate, the concentration of Cd was determined by differential pulse anodic stripping voltammetry (26).

11.g Cl, F, and S in the Andersen Ash by Extraction with Na_2CO_3_$NaHCO_3$ and Determination by Ion Chromatography

Table B-X gives the weights of Andersen ash samples used for extraction with $Na_2CO_3-NaHCO_3$ for determination of Cl, F, and S by ion chromatography after preparation according to Section 11.a. Andersen ash samples in Table B-X were extracted and analyzed by the procedure in Section 4.g for the less than 0.05 g TP ash samples.

12.h Analytical Procedures for Trace Elements in the XAD-2 Resin and Fly Ash Interlaboratory Samples

These samples were received after data for this study had been reported. The total weight of the XAD-2 resin sample (X2-1L) received was 2.96 g, and the total weight of the fly ash sample (IS-1Z) was 0.51 g.

With the exception of S and Cl, the XAD-2 resin sample was analyzed by procedures described in Section 8. S and Cl were determined semiquantitatively by the backup extraction-ion chromatography procedures described in Sections 8.h and 8.i. At that time the induction furnace, which measures total sulfur, was not functional because it lacked a backordered pedestal. Also, there was insufficient sample for Cl by the procedure in Section 8.j which gives total chlorine.

TABLE B-X

COMPOSITING SCHEME FOR ANDERSEN IMPACTOR FINE PARTICULATE FOR DETERMINING 3 ELEMENTS[a]

Composite of field tests	Composite of plates	Approximate particle size, μ	Extracted weight, mg
219A1+219A2	0_c+1+2+3[b]	>3	24.60
(See Above)	4+5[c]	1-3	-
(See Above)	6+7+8[b]	0-1	19.54
214A+215A +220A1+220A2 +221A1+221A2	0_c+1+2+3[c]	>3	-
(See Above)	4+5[c]	1-3	-
(See Above)	4+5[c]	0-1	-
322A	0_c+1+2+3[b]	>3	9.35
(See Above)	4+5[b]	1-3	5.10
(See Above)	6+7+8[b]	0-1	6.20
Filter blank	-	-	1.73[b]

---

[a] Cl, F, and S

[b] One-fourth of an Andersen stage filter was used.

[c] C, F, and S were not requested.

Because of the small sample weight, all elements in the fly ash sample (IS-1Z) were determined by microchemical techniques described in Section 7.a.

13 Quality Control

See Tables B-XI through B-XVI for results of NBS reference material determined concurrently with the samples.

TABLE B-XI

REFERENCE MATERIAL 1632 CONCURRENTLY DETERMINED WITH THE COAL AND PYRITE SAMPLES FOR THE FLY ASH DISPOSAL AND GASEOUS EMISSION STUDIES AT KINGSTON DURING 1977

Element	This Work, μg/g[a]	Other Work, μg/g[b]
Al	17500(3) ± 500	18500(24)
Sb	3.6(6) ± 0.3	3.9 (24)
As	5.1(3) ± 0.1	6.5(24), 5.9(5)[c]
Ba	316(3) ± 13	352(24)
Be	1.62(5) ± 0.04	1.5(5)[d]
B	60.4(5) ± 5.0	47.0(30), 47.7(30), 47.7(30), 30(30), 43(30)
Ca	4233(3) ± 416	4300(24)
Cd	-	0.19(5)[c]
Cl	885(5) ± 123	890(24), 290(31)
Cr	19.2(5) ± 0.3	19.7(24), 20.2(5)[c]
Co	<5, <5	5.7(24), 6(5)[d]
Cu	19.3(5) ± 0.8	18(5)[c]
F	89.4(4) ± 6.8	100(31), 84[e]
Fe	8250(5) ± 205	8400(24), 8700(5)[c]
Pb	40.0(5) ± 9.7	30(5)[c]
Mg	1200(3) ± 0	2000(24)
Mn	43.3(3) ± 0.6	43(24), 40(5)[c]
Hg	0.10(3) ± 0	0.12(5)[c]
Ni	14.5(5) ± 0.8	18(24), 15(5)[c]
K	2600(3) ± 153	2800(24)
Se	3.3(3) ± 0.3	3.4(24), 2.9(5)[c]
Si	37600(3) ± 4500	32000(24)[d]
Ag	-	≤ 0.01[d]
Na	412(3) ± 34	414(24)
S	-	1.28%(34)
Tl	-	0.59[c]
Ti	1000(3) ± 56	1100(24), 800(5)[d]
V	36.3(5) ± 1.1	36(24), 35(5)[c]
Zn	37.6(5) ± 1.5	30(24), 37(5)[c]

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[a] Mean (number of values) ± standard deviation.
[b] Reference numbers in parentheses.
[c] NBS certified value.
[d] NBS value for information only.
[e] Value obtained by Bituminous Coal Research.

TABLE B-XII

ELEMENTAL CONCENTRATIONS IN THE NBS COAL FLY ASH STANDARD REFERENCE MATERIAL 1633 CONCURRENTLY DETERMINED WITH ESP, MECHANICAL COLLECTOR AND BOTTOM ASH SAMPLES FOR THE FLY ASH DISPOSAL AND GASEOUS EMISSION STUDIES AT KINGSTON DURING 1977

Element	This Work, μg/g[a]	Other Work, μg/g[b]
Al	125000(7) ± 0	127000(24), 121000(33), 126000(33)
Sb	6.1(7) ± 0.9	6.7(24)
As	58.4(9) ± 2.9	58(24), 61(5)[c]
Ba	2560(7) ± 80	2700(24), 2900(32), 2510(33), 2300(33)
Be	11.9(9) ± 0.4	12(5)[d], 12.3(32), 12.6(33)
B	520(9) ± 20	490(30), 492(30), 497(30), 434(30), 500(30)
Ca	45300(7) ± 600	47000(24), 43000(33), 50000(33)
Cd	-	1.45(5)[c], 1.6(30), 1.3(32), 1.7(33)
Cl	43.8(9) ± 2.5	42(24), 42(31)
Cr	124(9) ± 4	127(24), 131(5)[c], 132(32), 118(33), 120(33)
Co	58.6(7) ± 4.8	41.5(24), 38(5)[d], 42(33)
Cu	132(9) ± 3	128(5)[c], 124(32), 119(33)
F	194(4) ± 25 (#78-32) 68(6) ± 9 (#78-33)	188 (#78-32), 59 (#78-33)
Fe	58200(9) ± 2300	62000(24), 60000(33), 62000(33)
Pb	110(9) ± 10	75(24), 70(5)[c], 82(32), 78(33)
Mg	13500(7) ± 400	18000(24), 12000(33)
Mn	517(7) ± 10	496(24), 493(5)[c], 520(32), 499(33), 477(33)
Hg	0.21(7) ± 0.006	0.14(5)[c]
Ni	117(9) ± 4	98(24), 98(5)[c], 100(33)
K	15400(7) ± 1250	16100(24), 17100(33), 17000(33)
Se	11.2(6) ± 1.7	10.2(24), 9.4(5)[c], 10(33)

TABLE B-XII (CONTINUED)

Element	This Work, μg/g[a]	Other Work, μg/g[b]
Si	258000(7) ± 13000	210000(24)
Ag	-	-
Na	3170(7) ± 70	3200(24), 3100(33), 3200(21)
S	-	-
Tl	-	4[d]
Ti	7370(7) ± 200	7400(24), 6800(33), 7400(33)
V	227(9) ± 20	235(24), 214(5)[c], 201(32), 270(33), 201(33)
Zn	194(9) ± 5	216(24), 210(5)[c], 212(32), 201(33), 220(33)

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[a] Mean (number of values) ± standard deviation.
[b] Reference numbers in parentheses.
[c] NBS certified value.
[d] NBS value for information only.
[e] Value obtained by Bituminous Coal Research for designated coal ash refuse samples split with TVA.

TABLE B-XIII

ELEMENTAL CONCENTRATIONS IN THE NBS COAL FLY ASH STANDARD REFERENCE MATERIAL 1633 CONCURRENTLY DETERMINED WITH ASH SAMPLES FROM THE TOTAL PARTICULATE TRAIN, SASS TRAIN, BRINK IMPACTOR, AND ANDERSEN IMPACTOR FOR THE GASEOUS EMISSION STUDY AT KINGSTON DURING 1977

Element	This Work, µg/g[a]	Other Work, µg/g[b]
Al	104900(12) ± 8500	127,000(24), 121,000(33), 126,000(33)
Sb	4.6(12) ± 0.8	6.7(24)
As	65.5(12) ± 16.7	58(24), 61(5)[c]
Ba[e]	1600(12) ± 254	2700(24), 2900(32), 2510(33), 2300(33)
Be	11(12) ± 1.4	12(5)[d], 12.3(32), 12.6(33)
B	418(12) ± 89	490(30), 492(30), 497(30), 434(30),
Ca	41100(12) ± 5400	47000(24), 43000(33), 50000(33)
Cd[e]	0.48(6) ± 0.19	1.45(5)[c], 1.6(30), 1.3(32), 1.7(33)
Cl	37.2(5) ± 7.8	42(24), 42(31)
Cr	107(12) + 17	127(24), 131(5)[c], 132(32), 118(33), 120(33)
Co	44.5(12) ± 3.2	41.5(24), 38(5)[d], 42(33)
Cu	126(12) ± 15	128(5)[c], 124(32), 119(33)
F	29.1(6) ± 3.8	-
Fe	57500(12) ± 3000	62000(24), 60000(33), 62000(33)
PP	77.5(12) ± 17.1	75(24), 70(5)[c], 82(32), 78(33)
Mg	13000(12) ± 2400	18000(24), 12000(33)
Mn	450(12) ± 30	496(24), 493(5)[c], 520(32), 499(33), 477(33)
Hg	0.16(9) ± 0.05	0.14(5)[c]
Ni	106(12) ± 12.5	98(24), 98(5)[c], 100(33)
K	11700(12) ± 2000	16100(24), 17100(33), 17000(33)
Se	7.4(12) ± 3.1	10.2(24), 9.4(5)[c], 10(33)

TABLE B-XIII (CONTINUED)

Element	This Work, µg/g[a]	Other Work, µg/g[b]
Si	-	210000(24)
Ag	-	-
Na	3100(12) ± 680	3200(24), 3100(33), 3200(21)
S	8700(6) ± 900	-
Tl	-	4[d]
Ti	6300(12) ± 280	7400(24), 6800(33), 7400(33)
V	210(12) ± 21	235(24), 214(5)[c], 201(32), 270(33), 201(33)
Zn	236(12) ± 26	216(24), 210(5)[c], 212(32), 201(33), 220(33)

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[a] Mean (number of values) ± standard deviation.
[b] Reference numbers in parentheses.
[c] NBS certified value.
[d] NBS value for information only.
[e] Raw data for Ba and Cd in samples were corrected to literature value by multiplying by 27/16 and 1.45/0.48, respectively.

TABLE B-XIV

ELEMENTAL CONCENTRATIONS IN THE NBS COAL STANDARD REFERENCE MATERIAL 1632 CONCURRENTLY DETERMINED WITH THE XAD-2 RESIN SAMPLES FROM THE SASS TRAIN FOR THE GASEOUS EMISSION STUDIES AT KINGSTON DURING 1977

Element	This Work, μg/g[a]	Other Work, μg/g[b]
Al	15200	18500(24)
Sb	(See Table XI)	3.9(24)
As	(See Table XI)	6.5(24), 5.9(5)[b]
Ba	100	352(24)
Be	1.3	1.5(5)[c]
B	33	47.0(30), 47.7(30), 47.7(3), 30(30), 43(30)
Ca	5100	4300(24)
Cd[e]	0.071	0.19(5)[b]
Cl	(See Table XIII)	890(24), 290(31)
Cr	16.7	19.7(24), 20.2(5)[b]
Co	(See Table XI)	5.7(24), 6(5)[c]
Cu	16.5	18(5)[b]
F	-	100(31), 84[d]
Fe	7900	8400(24), 8700(5)[b]
Pb	27	30(5)[b]
Mg	2200	2000(24)
Mn	40	43(24), 40(5)[b]
Hg	(See Table XI)	0.12(5)[b]
Ni	12.5	18(24), 15(5)[c]
K	1800	2800(24)
Se	(See Table XI)	3.4(24), 2.9(5)[b]
Si	-	32000(24)[c]
Ag	-	≤ 0.01[c]
Na	384	414(24)
S	-	1.28%(34)
Tl	-	0.59[b]
Ti	830	1100(24), 800(5)[c]
V	29	36(24), 35(5)
Zn	36	30(24), 37(5)[b]

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[a] Reference numbers in parentheses.
[b] NBS certified value.
[c] NBS value for information only.
[d] Value obtained by Bituminous Coal Research
[e] Raw data for Ba, K, and Cd in samples were corrected to literature value by multiplying by 352/100, 28/18, and 0.19/0.071, respectively.

TABLE B-XV

ELEMENTAL CONCENTRATIONS IN THE NBS COAL STANDARD REFERENCE MATERIAL 1632 CONCURRENTLY DETERMINED WITH THE INTERLABORATORY XAD-2 RESIN SAMPLE FOR THE GASEOUS EMISSION STUDY AT KINGSTON DURING 1977

Element	This Work, μg/g[a]	Other Work, μg/g[b]
Al	10100(2) ± 1630	18,500 (24)
Sb	(See Table XI)	3.9 (24)
As	(See Table XI)	6.5(24), 5.9(5)[c]
Ba	118(2) ± 4	352(24)
Be	1.30(2)± 0.16	1.5(5)[d]
B	20.4(2) ± 6.2	47.0(30), 47.7(30), 30(30), 43(30)
Ca	3380(2) ± 42	4300(24)
Cd	0.20(2) ± 0.09	0.19(5)[c]
Cl	(See Table XIII)	890(24), 290(31)
Cr	15.6(2) ± 1.2	19.7(24), 20.2(5)[c]
Co	(See Table XI)	5.7(24), 6(5)[d]
Cu	15.8(2) ± 1.5	18(5)[c]
F	-	100(31), 84[e]
Fe	6380(2) ± 670	8400(24), 8700(5)[c]
Pb	28.8(2) ± 0.2	30(5)[c]
Mg	866(2) ± 128	2000(24)
Mn	33.2(2) ± 4.7	43(24), 40(5)[c]
Hg	(See Table XI)	0.12(5)[c]
Ni	12.6(2) ± 1.3	18(24), 15(5)[c]
K	1510(2) ± 130	2800(24)
Se	(See Table XI)	3.4(24), 2.9(5)[c]
Si	-	32000(24)[d]
Ag	-	≤ 0.01[d]
Na	420,1520	414(24)
S	-	1.28%(34)
Tl	-	0.59[c]
Ti	658(2) ± 87	1100(24), 800(5)[d]
V	27.8(2) ± 3.2	36(24), 35(5)
Zn	43.7(2) ± 7.2	30(24), 37(5)[c]

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[a] Mean (number of values) ± standard deviation.
[b] Reference numbers in parentheses.
[c] NBS certified value.
[d] NBS value for information only.
[e] Value obtained by Bituminous Coal Research.

TABLE B-XVI

ELEMENTAL CONCENTRATIONS IN THE NBS COAL FLY ASH STANDARD REFERENCE MATERIAL 1633 CONCURRENTLY DETERMINED WITH THE INTERLABORATORY FLY ASH SAMPLE FOR THE GASEOUS EMISSION STUDY AT KINGSTON DURING 1977

Element	This Work, μg/g[a]	Other Work, μg/g[b]
Al	94000(3) ± 8700	127000(24), 121000(33), 126000(33)
Sb	(See Table XIII)	6.7(24)
As	(See Table XIII)	58(24), 61(5)[c]
Ba[f]	1390(3) ± 400	2700(24), 2900(32), 2510(33), 2300(33)
Be	11.0(3) ± 0.1	12(5)[d], 12.3(32), 12.6(33)
B[f]	199(3) ± 139	490(30), 492(30), 497(30), 434(30), 500(30)
Ca[f]	28400(3) ± 6900	47000(24), 43000(33), 50000(33)
Cd	0.95(3) ± 016	1.45(5)[c], 1.6(30), 1.3(32), 1.7(33)
Cl	(See Table XIII)	42(24), 42(31)
Cr	97(3) ± 2	127(24), 131(5)[c], 132(32), 118(33), 120(33)
Co	(See Table XIII)	41.5(24), 38(5)[d], 42(33)
Cu	119(3) ± 2	128(5)[c], 124(32), 119(33)
F	(See Table XIII)	188 (#78-32), 59 (#78-33)
Fe	54000(3) ± 2200	62000(24), 60000(33), 62000(33)
Pb	68(3) ± 5	75(24), 70(5)[c], 82(32), 78(33)
Mg[f]	7150(3) ± 2180	18000(24), 12000(33)
Mn	354(3) ± 53	496(24), 493(5)[c], 520(32), 499(33), 477(33)
Hg[f]	0.064(2) ± 0.008	0.14(5)[c]
Ni	102(3) ± 2	98(24), 98(5)[c], 100(33)
K[f]	9410(3) ± 640	16100(24), 17100(33), 17000(33)
Se	(See Table XIII)	10.2(24), 9.4(5)[c], 10(33)

TABLE B-XVI (CONTINUED)

Element	This Work, μg/g[a]	Other Work, μg/g[b]
Si	-	210000(24)
Ag	-	-
Na[f]	1630(3) ± 327	3200(24), 3100(33), 3200(21)
S	-	-
Tl	-	4[d]
Ti	6240(3) ± 275	7400(24), 6800(33), 7400(33)
V	211(3) ± 2	235(24), 214(5)[c], 201(32), 270(33), 201(33)
Zn	196(3) ± 21	216(24), 210(5)[c], 212(32), 201(33), 220(33)

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[a] Mean (number of values) ± standard deviation.
[b] Reference numbers in parentheses.
[c] NBS certified value.
[d] NBS value for information only.
[e] Value obtained by Bituminous Coal Research for designated coal ash refuse samples split with TVA.
[f] Raw data for Ba, B, Ca, Mg, K, Na, and Hg in samples were corrected to literature values by multiplying by 27/14, 492/199, 47/28.4, 120/71.5, 161/94.1, 32/13, and 14/6.4, respectively.

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